Supporting Information

Nickel-Catalyzed Reductive Transamidation of Secondary Amides with Nitroarenes

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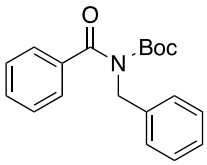
General Considerations

(A) General Analytical Information.

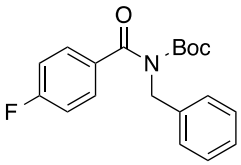
Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signal of tetramethylsilane (TMS) added into the deuterated chloroform ($CDCl_3$, 0.00 ppm), the signal of residual dichloromethane in deuterated dichloromethane (CD_2Cl_2, 5.32 ppm), or the signal of residual dimethyl sufloxide in dimethyl-d_6 sufloxide (DMSO-d_6, 2.50 ppm).[1] Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextet, m = multiplet, ovrlp = overlap, br = broad), coupling constants, and integration. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm), or DMSO-d_6 (39.52 ppm)[1] and were obtained with complete ^{1}H decoupling. All ^{19}F NMR spectra were reported in ppm relative to hexafluorobenzene as an internal standard (-164.9 ppm, with reference to $CFCl_3$ at 0 ppm) and were obtained with complete ^{1}H decoupling. All gas chromatography (GC) analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All gas chromatography-mass spectrometry (GC-MS) analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. High-resolution mass spectra (HRMS) by electrospray ionization (ESI) method were performed at the EPFL ISIC Mass Spectroscopy Service with a Micro Mass QTOF Ultima spectrometer. Intra-red (IR) spectra were recorded on solid or liquid samples on a Varian 800 FT-IR spectrometer using attenuated total reflectance (ATR) sampling techniques. Melting points (Mp) of solid compounds were measured using Büchi Model B-540 melting point apparatus.

(B) General Reagent Information.

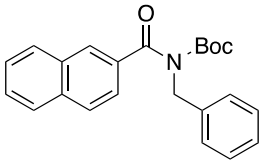
Unless otherwise noted, all chemicals were used as received without further purifications. Anhydrous *N*-methylpyrrolidone (NMP) (99.8% purity, in Sure-Seal bottle), zinc powder (Zn, >98% purity), manganese powder (Mn, 99.99% purity), and chlorotrimethylsilane (TMSCl, ≥98% purity) were purchased from Aldrich Chemical Co.. Nickel(II) chloride ethylene glycol dimethyl ether complex ($Ni(glyme)Cl_2$) was purchased from ABCR GmbH& Co. KG. 1,10-Phenanthroline (phen) was purchased from Acros Chemicals. Iodotrimethylsilane (TMSI, ≥95% purity), 2,2′:6′,2″-terpyridine (terpyridine), and 4,7-dimethyl-1,10-phenanthroline were purchased from TCI Chemicals. While low molecular weight organic compounds containing multiple nitro groups are potentially explosive, the nitroarenes used in this study contain only one nitro group and we encountered no safety issues in their preparation and uses. The following known starting materials (amides and nitroarenes) were prepared according to the literature procedures:[2-7]



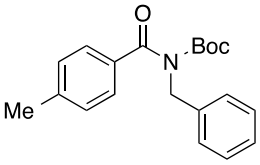
tert-butyl benzoyl(benzyl)carbamate[2]



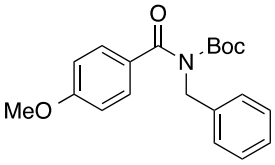
tert-butyl benzyl(4-fluorobenzoyl)carbamate[2]



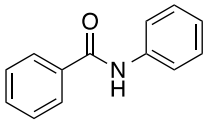
tert-butyl (2-naphthoyl)(benzyl)carbamate[3]



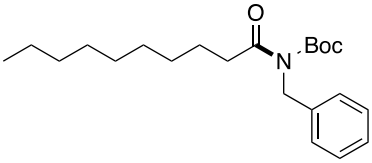
tert-butyl benzyl(4-fluorobenzoyl)carbamate[3]



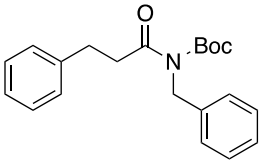
tert-butyl benzyl(4-fluorobenzoyl)carbamate[3]



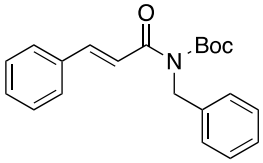
N-phenylbenzamide[4]



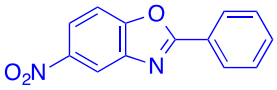
tert-butyl benzyl(decanoyl)carbamate[5]



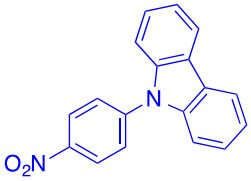
tert-butyl benzyl(3-phenylpropanoyl)carbamate[5]



tert-butyl benzyl(cinnamoyl)carbamate[5]



5-nitro-2-phenylbenzo[*d*]oxazole[6]



9-(4-nitrophenyl)-9*H*-carbazole[7]

(C) General Manipulation Considerations.

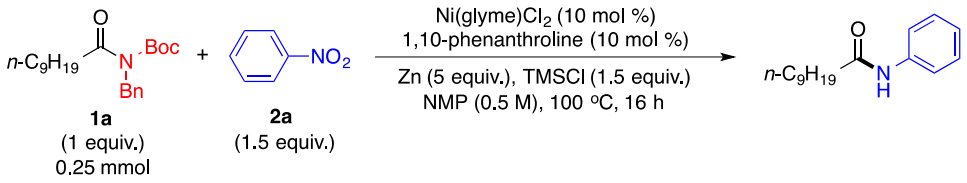
All manipulations for the nickel-catalyzed reductive transamidation with nitroarenes were set up in a 30 mL Teflon-screw capped test tubes under an inert nitrogen (N_2) atmosphere using glove-box techniques. The test tubes were then sealed with airtight electrical tapes and the reaction mixtures were stirred in a preheated oil-bath. Flash column chromatography was performed using silica gel (Silicycle, ultra pure grade). Preparative thin-layer chromatography (preparative TLC) was performed using preparative TLC plate (Merck Millipore, TLC Silica gel 60 F_{254}, 20 x 20 cm, catalogue number: 1.05715.0001) in a developing tank. Notably, the TLC plates used for the purification of amide products were washed with hexanes/triethylamine solution (volume ratio ~20:1) prior to use in order to minimize the product loss. The eluents for column chromatography and preparative TLC were presented as ratios of solvent volumes. Yields reported in the publication are of isolated materials unless otherwise noted. All new starting materials and amide products were characterized by ^{1}H and ^{13}C NMR spectroscopies, high-resolution mass spectrometry (HRMS), infra-red (IR) spectroscopy, and melting point (Mp) measurement (for soild compounds). All known amide products were characterized by ^{1}H and ^{13}C NMR spectroscopies (the spectra were compared with the reported data if provided), and most of them were further characterized by infra-red spectroscopy.

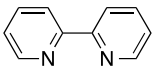
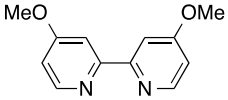
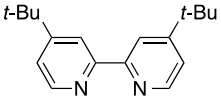
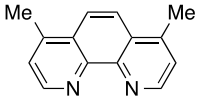
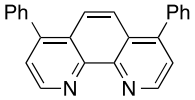
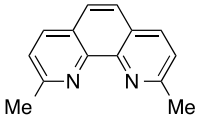
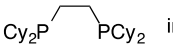
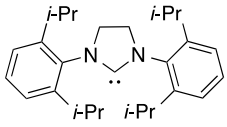
Supplementary Data

(A) Optimization of Reaction Conditions for Nickel-Catalyzed Reductive Transamidation of Alkyl Amide with Nitrobenzene.

Boc-activated secondary alkyl amide, *tert*-butyl benzyl(decanoyl)carbamate (**1a**), and nitrobenzene ($PhNO_2$, **2a**) were used as the model substrates of alkyl amide and nitroarene, respectively. After the screening of reaction parameters, we found that the reductive coupling of **1a** with **2a** proceeded smoothly at 100 ^oC to yield the desired amide product, *N*-phenyl decanamide, in 80% yield in the presence of Zn reductant (5 equiv), TMSCl additive (2 equiv), NMP solvent (0.5 M of **1a**), and Ni(glyme)Cl_2 (10 mol %)/phen (10 mol %) as the catalyst system (Table S1, entry 1). The use of other ligands (Table S1, entries 2-9), nickel catalysts (Table S1, entries 10-13), additives (Table S1, entries 16-19), reductant (Mn, Table S1, entry 22), and solvents (Table S1, entries 26 and 27) led to diminishment in yields. The variation of loadings of Ni(glyme)Cl_2 (Table S1, entries 14 and 15), TMSCl (Table S1, entries 20 and 21), Zn (Table S1, entries 23-25), and **2a** (Table S1, entries 29 and 30), as well as the change in solvent volume (Table S1, entry 28) or reaction temperatures (Table S1, entries 31 and 32), also resulted in drop of yields. The use of other transition metal catalysts (Fe, Co, Cu. Mn) resulted in much lower yields of product (Table S1, entries 33-36). Control experiments demonstrated that TMSCl, Ni(glyme)Cl_2 catalyst, and phen ligands were essential to promote the reductive transmidation (Table S1, entries 37-40). The reaction with aniline only gave a low yield of amide (Table S1, entries 41 and 42), suggesting that aniline is unlikely the active intermediate in transamidation.

Table S1. Optimizations of Nickel-Catalyzed Reductive Transamidation of Boc-activated Secondary Alkyl Amide with Nitrobenzene



entry	Variations from 'standard conditions'	GC yield of amide (%)[a]
1	no variation	80
2	 instead of phen	77
3	 instead of phen	60
4	 instead of phen	67
5	 instead of phen	63
6	 instead of phen	78
7	 instead of phen	53
8	 instead of phen	61
9	 instead of phen	55
10	$Ni(diglyme)Br_2$ instead of $Ni(glyme)Cl_2$	71
11	$NiBr_2$ instead of $Ni(glyme)Cl_2$	67
12	$NiCl_2$ instead of $Ni(glyme)Cl_2$	70
13	$NiCl_2 \cdot 6H_2O$ instead of $Ni(glyme)Cl_2$	<5
14	$Ni(glyme)Cl_2$ (15 mol %), phen (15 mol %) instead of $Ni(glyme)Cl_2$ (10 mol %), phen (10 mol %)	69
15	$Ni(glyme)Cl_2$ (5 mol %), phen (5 mol %) instead of $Ni(glyme)Cl_2$ (10 mol %), phen (10 mol %)	65

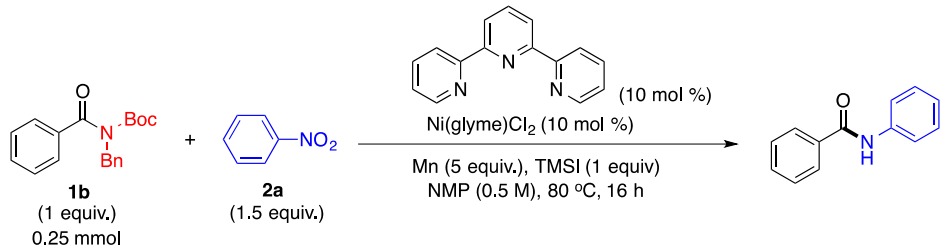
entry	Variations from 'standard conditions'	GC yield of amide (%)[a]
16	TMSBr instead of TMSCl	73
17	TMSI instead of TMSCl	67
18	TESCl instead of TMSCl	71
19	$(EtO)_3SiCl$ instead of TMSCl	79
20	TMSCl (1 equiv) instead of (1.5 equiv)	75
21	TMSCl (2 equiv) instead of (1.5 equiv)	72
22	Mn instead of Zn	47
23	Zn (4 equiv) instead of (5 equiv)	66
24	Zn (4.5 equiv) instead of (5 equiv)	74
25	Zn (5.5 equiv) instead of (5 equiv)	75
26	DMA instead of NMP	74
27	DMF instead of NMP	70
28	NMP (0.75 mL) instead of (0.5 mL)	60
29	$PhNO_2$ (1.3 equiv) instead of (1.5 equiv)	66
30	$PhNO_2$ (1.7 equiv) instead of (1.5 equiv)	74
31	90 °C instead of 100 °C	68
32	120 °C instead of 100 °C	37
33	$FeBr_2$ (10 mol %) instead of $Ni(glyme)Cl_2$	25
34	$CoBr_2$ (10 mol %) instead of $Ni(glyme)Cl_2$	27
35	$CuBr_2$ (10 mol %) instead of $Ni(glyme)Cl_2$	9
36	$Mn(OTf)_2$ (10 mol %) instead of $Ni(glyme)Cl_2$	7
	Control experiments:	
37	no TMSCl	<5[b]
38	no phen	62
39	no $Ni(glyme)Cl_2$	6[b]
40	no $Ni(glyme)Cl_2$ and phen	0[b]
41	$PhNH_2$ instead of $PhNO_2$	28
42	$PhNH_2$ (1.5 equiv) instead of $PhNO_2$; Zn (3 equiv) instead of (5 equiv); $Zn(OTf)_2$ (2 equiv) added; no TMSCl	<5

[a] Corrected GC yield using *n*-dodecane as internal standard. [b] Incomplete conversion.

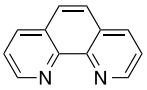
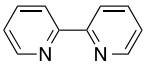
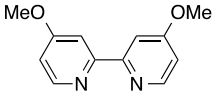
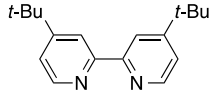
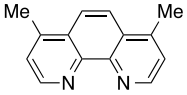
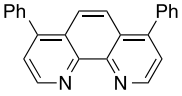
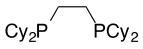
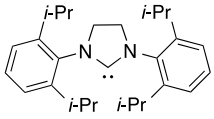
(B) Optimization of Reaction Conditions for Nickel-Catalyzed Reductive Transamidation of Aryl Amide with Nitrobenzene.

Boc-activated secondary aryl amide, *tert*-butyl benzoyl(benzyl)carbamate (**1b**), and nitrobenzene (**2a**) were used as the model substrates of aryl amide and nitroarene, respectively. Initially, we applied the optimal conditions in Table S1 (Table S1, entry 1) for the reactions, and the desired product, *N*-phenyl benzamide, was obtained in 63% yield (Table S2, entry 1). After the subsequent screening of reaction parameters, we found that the reductive coupling of **1b** with **2a** proceeded smoothly at 80 ^{o}C to yield *N*-phenyl benzamide in 88% yield in the presence of Mn reductant (5 equiv), TMSI additive (1 equiv), NMP solvent (0.5 M of **1b**), and Ni(glyme)Cl_2 (10 mol %)/terpyridine (10 mol %) as the catalyst system (Table S2, entry 2). The use of other ligands (Table S2, entries 3-10), nickel catalysts (Table S2, entries 11 and 12), additives (Table S2, entries 15-17), reductant (Zn, Table S2, entry 20), and solvent (Table S2, entry 23) led to diminishment in yields. The variation of loadings of Ni(glyme)Cl_2 (Table S2, entries 13 and 14), TMSI (Table S2, entries 18 and 19), Mn (Table S2, entries 21 and 22), and **2a** (Table S2, entries 25 and 26), as well as the change in solvent volume (Table S2, entry 24) or reaction temperatures (Table S2, entries 27 and 28), also resulted in drop of yields. The use of other transition metal catalysts (Fe, Co, Cu. Mn) resulted in modest product yields (Table S2, entries 29-32). Control experiments demonstrated that TMSI, Ni(glyme)Cl_2 catalyst, and terpyridine ligand were essential to promote the reductive transmidation (Table S2, entries 33-36). The reaction with aniline only gave a low yield of amide (Table S2, entry 37), suggesting that aniline is unlikely the active intermediate in transamidation.

Table S2. Optimizations of Nickel-Catalyzed Reductive Transamidation of Boc-activated Secondary Aryl Amide with Nitrobenzene



1b (1 equiv.) 0.25 mmol + **2a** (1.5 equiv.)

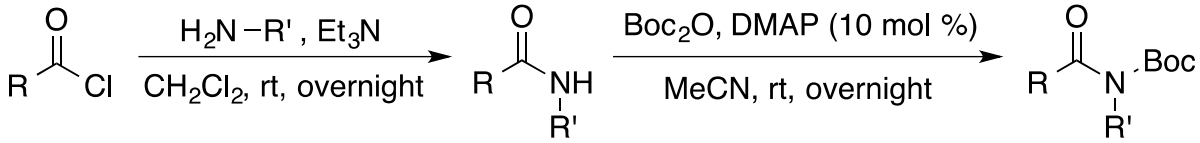
entry	Variations from 'standard conditions'	GC yield of amide (%)[a]
1	**Method A** was used instead of **Method B**	63
2	no variation	88
3	 instead of terpyridine	69
4	 instead of terpyridine	73
5	 instead of terpyridine	60
6	 instead of terpyridine	77
7	 instead of terpyridine	68
8	 instead of terpyridine	54
9	 instead of terpyridine	67
10	 instead of terpyridine	64
11	$Ni(diglyme)Br_2$ instead of $Ni(glyme)Cl_2$	80
12	$NiCl_2$ instead of $Ni(glyme)Cl_2$	73
13	$Ni(glyme)Cl_2$ (15 mol %) instead of (10 mol %)	82

entry	Variations from 'standard conditions'	GC yield of amide (%)[a]
14	$Ni(glyme)Cl_2$ (5 mol %) instead of (10 mol %)	79
15	TMSBr instead of TMSI	84
16	TMSCl instead of TMSI	83
17	TESCl instead of TMSI	79
18	TMSI (0.5 equiv) instead of (1 equiv)	83
19	TMSI (1.5 equiv) instead of (1 equiv)	82
20	Zn instead of Mn	17[b]
21	Mn (4.5 equiv) instead of (5 equiv)	83
22	Mn (5.5 equiv) instead of (5 equiv)	81
23	DMA instead of NMP	81
24	NMP (0.75 mL) instead of (0.5 mL)	86
25	$PhNO_2$ (1.3 equiv) instead of (1.5 equiv)	73
26	$PhNO_2$ (1.7 equiv) instead of (1.5 equiv)	80
27	60 °C instead of 80 °C	83
28	100 °C instead of 80 °C	82
29	$FeBr_2$ instead of $Ni(glyme)Cl_2$	61
30	$CoBr_2$ instead of $Ni(glyme)Cl_2$	46
31	$CuBr_2$ instead of $Ni(glyme)Cl_2$	19
32	$MnCl_2$ instead of $Ni(glyme)Cl_2$	12
	Control experiments;	
33	no TMSI	62
34	no terpyridine	71
35	no $Ni(glyme)Cl_2$	15[b]
36	no $Ni(glyme)Cl_2$ and terpyridine	15[b]
37	$PhNH_2$ instead of $PhNO_2$	36

[a] Corrected GC yield using *n*-dodecane as internal standard. [b] Incomplete conversion.

Experimental Section

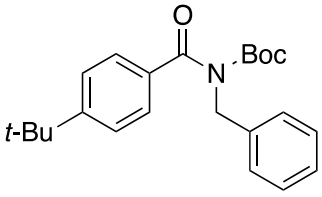
Synthesis of Starting Materials:



General Procedures for the Synthesis of Boc-Activated Secondary Amides (General Procedure A).

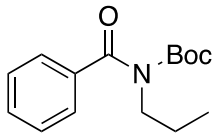
Step 1: An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with dichloromethane solvent (CH_2Cl_2), amide, and triethylamine (Et_3N). The reaction mixture was stirred at room temperature, and acyl chloride was slowly added in a few portions into the reaction mixture. The resulting mixture was stirred at room temperature overnight. After the reaction, the organic fraction was washed with dilute HCl solution (~1 M, ~100 mL), followed by saturated NaOH solution (~30 mL), and finally saturated NaCl solution (~50 mL). The organic fraction was dried with $MgSO_4$ powder and then dried *in vacuo* with the aid of a rotary evaporator to obtain the residue as a secondary amide.

Step 2: All secondary amide prepared from step 1 was transferred into an oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, and acetonitrile solvent (MeCN), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 10 mol %), and di-*tert*-butyl dicarbonate (Boc_2O) were then added. The resulting mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was dried *in vacuo*, and the crude product was washed with ethyl acetate (EtOAc, ~100 mL) and dilute HCl solution (~1 M, ~100 mL). The organic fraction was further washed with saturated $NaHCO_3$ solution (~100 mL) followed by saturated NaCl solution (~50 mL). The organic fraction was then concentrated *in vacuo*, and the residue was purified by flash chromatography with silica gel (without prior washing with Et_3N/hexanes) using a mixture of hexanes/EtOAc as an eluent to afford the activated, Boc-activated secondary amide.

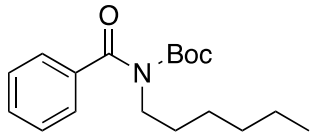


***tert*-Butyl Benzyl(4-(*tert*-butyl)benzoyl)carbamate (S1).** Following the general procedure A, the title compound was prepared by (i) using 4-*tert*-butylbenzoyl chloride (1 equiv, 1.2 mL, 6.0 mmol), benzylamine (1.2 equiv, 7.2 mmol, 0.77 mL), Et_3N (1.5 equiv, 9 mmol, 1.23 mL), and CH_2Cl_2 (100 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 1.4 mL), DMAP (73 mg), and MeCN (100 mL) to prepare activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (1.39 g, 63%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.50-7.44 (ovrlp, 4 H), 7.42 (d, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* =

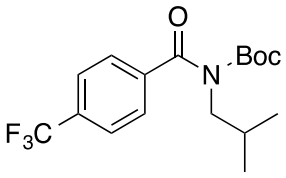
7.6 Hz, 2 H), 7.28 (t, *J* = 7.3 Hz, 1 H), 4.97 (s, 2 H), 1.35 (s, 9 H), 1.14 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 173.4, 155.2, 153.9, 138.7, 135.3, 128.8, 128.2, 127.8, 127.6, 125.4, 83.3, 49.2, 35.3, 31.3, 27.5. **HRMS** (ESI): Calcd for $C_{23}H_{29}NO_3Na$ [M+Na]: 390.2045; Found: 390.2045. **IR** (neat, cm^{-1}): 1716, 1681, 1359, 1235, 1152, 970, 850. Mp: 66-68 ^oC.



***tert*-Butyl Benzoyl(propyl)carbamate (S2).** Following the general procedure A, the title compound was prepared by (i) using benzoyl chloride (1 equiv, 1.2 mL, 10 mmol), *n*-propylamine (1.2 equiv, 12 mmol, 0.99 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (150 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.4 mL), DMAP (122 mg), and MeCN (150 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a yellow liquid (855 mg, 32%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.53-7.46 (ovrlp, 3 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 3.77 (t, *J* = 7.3 Hz, 2 H), 1.73 (hex, *J* = 7.4 Hz, 2 H), 1.17 (s, 9 H), 0.99 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 173.4, 153.9, 138.8, 131.1, 128.4, 127.7, 82.9, 47.6, 27.5, 22.5, 11.6. **HRMS** (ESI): Calcd for $C_{15}H_{21}NO_3Na$ [M+Na]: 286.1419; Found: 286.1426. **IR** (neat, cm^{-1}): 1729, 1669, 1336, 1233, 1139, 1071.

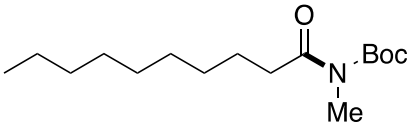


***tert*-Butyl Benzoyl(hexyl)carbamate (S3).** Following the general procedure A, the title compound was prepared by (i) using benzoyl chloride (1 equiv, 1.2 mL, 10 mmol), *n*-hexylamine (1.2 equiv, 12 mmol, 1.6 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (150 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.4 mL), DMAP (122 mg), and MeCN (150 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a yellow liquid (1.48 g, 48 %). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.50 (d, *J* = 7.7 Hz, 2 H), 7.45 (t, *J* = 7.9 Hz, 1 H), 7.37 (t, *J* = 7.1 Hz, 2 H), 3.80 (t, *J* = 7.7 Hz, 2 H), 1.69 (qu, *J* = 6.9 Hz, 2 H), 1.40-1.27 (ovrlp, 6 H), 1.14 (s, 9 H), 0.89 (t, *J* = 6.3 Hz, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 173.1, 153.5, 138.2, 130.7, 127.9, 127.2, 82.6, 45.7, 31.4, 28.7, 27.3, 26.5, 22.5, 14.0. **HRMS** (ESI): Calcd for $C_{18}H_{27}NO_3Na$ [M+Na]: 328.1889; Found: 328.1879. **IR** (neat, cm^{-1}): 1729, 1671, 1337, 1138.

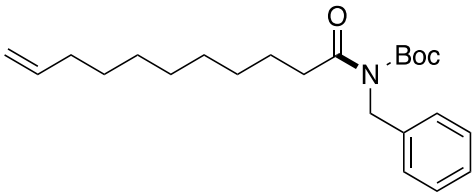


***tert*-Butyl Isobutyl(4-(trifluoromethyl)benzoyl)carbamate (S4).** Following the general procedure A, the title compound was prepared by (i) using 4-(trifluoromethy)benzoyl chloride (1 equiv, 12 mmol, 1.79 mL), isobutylamine (1.3 equiv, 15.6 mmol, 1.55 mL), Et_3N (1.5 equiv, 18 mmol, 2.5 mL), and

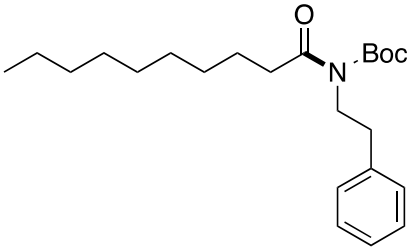
CH_2Cl_2 (200 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.9 mL), DMAP (146 mg), and MeCN (200 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (3.31 g, 80 %). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.70 (d, *J* = 8.2 Hz, 2 H), 7.63 (d, *J* = 8.1 Hz, 2 H), 3.68 (d, *J* = 7.3 Hz, 2 H), 2.20-2.06 (m, 1 H), 1.19 (s, 9 H), 0.98 (d, *J* = 6.7 Hz, 6 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 172.2, 153.9, 142.5, 132.6 (q, $^2J_{CF}$ = 32.3 Hz), 128.0, 125.6 (q, $^3J_{CF}$ = 15.1 Hz), 124.5 (q, $^1J_{CF}$ = 270.5 Hz), 83.8, 32.9, 28.7, 27.6, 20.5. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -66.0. **HRMS** (ESI): Calcd for $C_{17}H_{22}F_3NO_3Na$ [M+Na]: 368.1450; Found: 368.1448. **IR** (neat, cm^{-1}): 1737, 1658, 1327, 1237, 1169, 1107, 862, 763. Mp: 56-58 °C.



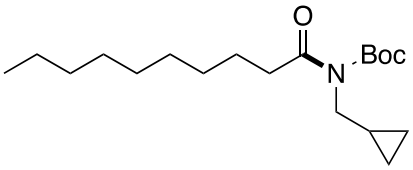
***tert*-Butyl Decanoyl(methyl)carbamate (S5).** Following the general procedure A, the title compound was prepared by (i) using decanoyl chloride (1 equiv, 20 mmol, 4.2 mL), methylamine (2 M solution in THF, 2 equiv, 40 mmol, 20 mL), Et_3N (1.5 equiv, 30 mmol, 4.2 mL), and CH_2Cl_2 (250 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.3 equiv, 5.7 mL), DMAP (244 mg), and MeCN (250 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale-brown liquid (3.78 g, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.13 (s, 3 H), 2.84 (t. *J* = 7.7 Hz, 2 H), 1.63 (qu. *J* = 7.1 Hz, 2 H), 1.53 (s, 9 H), 1.37-1.20 (ovrlp, 12 H), 0.88 (t. *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.4, 153.5, 82.8, 38.4, 32.0, 31.5, 29.6, 29.38, 29.37, 28.1, 25.3, 22.8, 14.2 (13 of 14 carbons observed). **HRMS** (ESI): Calcd for $C_{16}H_{31}NO_3Na$ [M+Na]: 308.2202; Found: 308.2192. **IR** (neat, cm^{-1}): 1733, 1699, 1314, 1143.



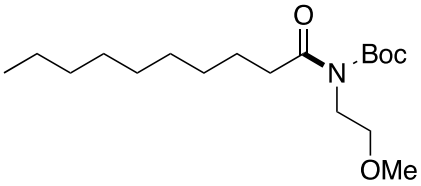
***tert*-Butyl Benzyl(undec-10-enoyl)carbamate (S6).** Following the general procedure A, the title compound was prepared by (i) using undec-10-enoyl chloride (1 equiv, 12 mmol, 2.6 mL), benzylamine (1.2 equiv, 14.4 mmol, 1.54 mL), Et_3N (1.5 equiv, 18 mmol, 2.5 mL), and CH_2Cl_2 (150 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.9 mL), DMAP (146 mg), and MeCN (150 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a yellow liquid (3.18 g, 71%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.32 (t. *J* = 7.4 Hz, 2 H), 7.28-7.23 (ovrlp, 3 H), 5.91-5.81 (m, 1 H), 5.06-5.00 (m, 1 H), 4.98-4.94 (m, 1 H), 4.90 (s, 2 H), 2.92 (t. *J* = 7.7 Hz, 2 H), 2.08 (q. *J* = 7.4 Hz, 2 H), 1.68 (qu. *J* = 7.2 Hz, 2 H), 1.44 (s, 9 H), 1.39-1.31 (ovrlp, 10 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 176.4, 153.6, 139.7, 139.3, 128.7, 127.8, 127.4, 114.4, 83.4, 47.7, 38.7, 34.3, 29.92, 29.86, 29.8, 29.6, 29.5, 28.1, 25.8. **HRMS** (ESI): Calcd for $C_{23}H_{35}NO_3Na$ [M+Na]: 396.2515; Found: 396.2519. **IR** (neat, cm^{-1}): 1733, 1697, 1368, 1146, 630.



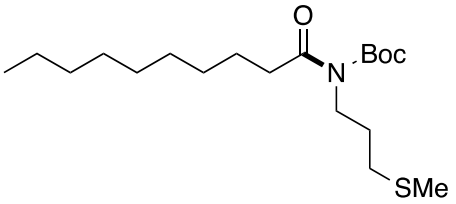
***tert*-Butyl Decanoyl(phenethyl)carbamate (S7).** Following the general procedure A, the title compound was prepared by (i) using decanoyl chloride (1 equiv, 10 mmol, 2.1 mL), 2-phenylethan-1-amine (1.2 equiv, 12 mmol, 1.5 mL), Et_3N (1.5 equiv, 15 mmol, 2.l mL), and CH_2Cl_2 (200 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.4 mL), DMAP (122 mg), and MeCN (250 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale-brown liquid (1.23 g, 33%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 6.6 Hz, 2 H), 7.21-7.17 (ovrlp, 3 H), 3.88 (t, *J* = 7.8 Hz, 2 H), 2.85-2.79 (ovrlp, 4 H), 1.62 (qu, *J* = 7.2 Hz, 2 H), 1.48 (s, 9 H), 1.34-1.23 (ovrlp, 12 H), 0.88 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.1, 153.1, 139.0, 129.0, 128.5, 126.4, 82.7, 46.1, 38.5, 35.1, 32.0, 29.6, 29.5, 29.4, 29.3, 28.0, 25.2, 22.7, 14.2. **HRMS** (ESI): Calcd for $C_{23}H_{37}NO_3$ Na [M+Na]: 398.2671; Found: 398.2668. **IR** (neat, cm^{-1}): 1732, 1695, 1368, 1143.



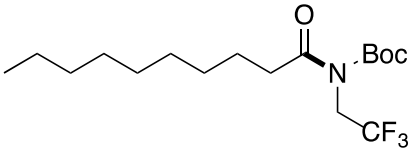
***tert*-Butyl (Cyclopropylmethyl)(decanoyl)carbamate (S8).** Following the general procedure A, the title compound was prepared by (i) using decanoyl chloride (1 equiv, 10 mmol, 2.1 mL), cyclopropylmethanamine (1.2 equiv, 12 mmol, 1.13 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (200 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.4 mL), DMAP (121 mg), and MeCN (250 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a brown liquid (1.43 g, 44%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.50 (d, *J* = 7.0 Hz, 2 H), 2.76 (t, *J* = 7.6 Hz, 2 H), 1.55 (qu, *J* = 6.8 Hz, 2 H), 1.46 (s, 9 H), 1.30-1.14 (ovrlp, 12 H), 1.08-0.97 (m, 1 H), 0.80 (t, *J* = 6.7 Hz, 3 H), 0.38-.31 (m, 2 H), 0.25-0.19 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.4, 153.6, 82.6, 48.6, 38.6, 32.0, 29.6, 29.38, 29.37, 28.1, 25.4, 22.8, 14.2, 10.7, 3.6 (15 of 16 carbons observed). **HRMS** (ESI): Calcd for $C_{19}H_{35}NO_3Na$ [M+Na]: 348.2515; Found: 348.2508. **IR** (neat, cm^{-1}): 1730, 1697, 1368, 1246, 1141.



***tert*-Butyl Decanoyl(2-methoxyethyl)carbamate (S9).** Following the general procedure A, the title compound was prepared by (i) using decanoyl chloride (1 equiv, 10 mmol, 2.1 mL), 2-methoxyethan-1-amine (1.2 equiv, 12 mmol. 1.05 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (200 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.4 mL), DMAP (121 mg), and MeCN (250 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale-brown liquid (1.31 g, 40%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.90 (t, *J* = 6.0 Hz, 2 H), 3.47 (t, *J* = 6.0 Hz, 2 H), 3.33 (s, 3 H), 2.82 (t, *J* = 7.4 Hz, 2 H), 1.62 (qu, *J* = 7.0 Hz, 2 H), 1.53 (s, 9 H), 1.34-1.23 (ovrlp, 12 H), 0.88 (t, *J* = 7.0 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.1, 153.3, 82.9, 70.5, 58.7, 43.4, 38.3, 31.9, 29.5, 29.33, 29.30, 28.0, 25.3, 22.7, 14.1 (15 of 16 carbons observed). **HRMS** (ESI): Calcd for $C_{18}H_{35}NO_4Na$ [M+H]: 352.2464; Found: 352.2465. **IR** (neat, cm^{-1}): 1733, 1693, 1368, 1350, 1143, 1121, 1077.



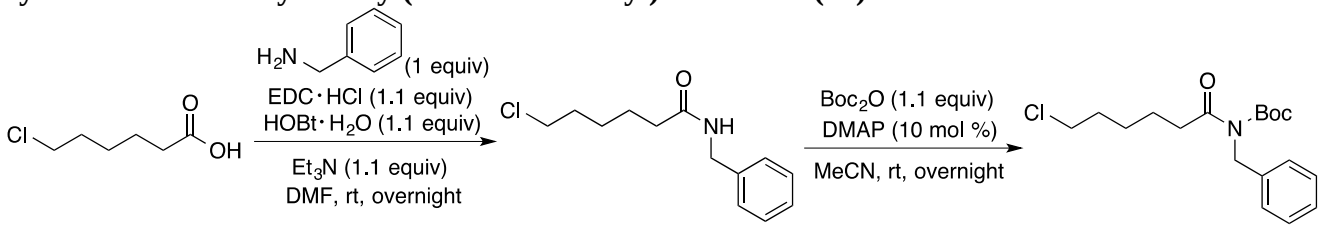
***tert*-Butyl Decanoyl(3-(methylthio)propyl)carbamate (S10).** Following the general procedure A, the title compound was prepared by (i) using decanoyl chloride (1 equiv, 10 mmol, 2.1 mL), 3-(methylthio)propan-1-amine (1.2 equiv, 12 mmol, 1.42 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (200 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.3 equiv, 2.4 mL), DMAP (121 mg), and MeCN (250 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale-brown, low-melting solid (900 mg, 25%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.69 (t, *J* = 7.1 Hz, 2 H), 2.75 (t, *J* = 7.4 Hz, 2 H), 2.44 (br s, 2 H), 2.05 (br s, 3 H), 1.75 (qu, *J* = 7.0 Hz, 2 H), 1.54 (t, *J* = 7.2 Hz, 2 H), 1.46 (s, 9 H), 1.29-1.14 (ovrlp, 12 H), 0.80 (t, *J* = 6.7 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.2, 153.3, 82.9, 43.8, 38.5, 32.0, 31.6, 29.6, 29.4, 28.24, 28.16, 25.3, 22.8, 15.4, 14.2 (15 of 17 carbons observed). **HRMS** (ESI): Calcd for $C_{19}H_{37}NO_3SNa$ [M+Na]: 382.2392; Found: 382.2396. **IR** (neat, cm^{-1}): 1732, 1695, 1368, 1253, 1142.



***tert*-Butyl Decanoyl(2,2,2-trifluoroethyl)carbamate (S11).** Following the general procedure A, the title compound was prepared by (i) using decanoyl chloride (1 equiv, 10 mmol, 2.1 mL), 2,2,2-trifluoroethan-1-amine (1.2 equiv, 12 mmol, 0.96 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (200 mL) to prepare the secondary amide, followed by (ii) using Boc_2O (1.1 equiv, 2.4 mL), DMAP (121 mg), and MeCN (250 mL) to prepare the activated amide. The crude product was purified using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a colorless liquid (2.53 g, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.35 (q, $^3J_{CF}$ = 8.6 Hz, 2 H), 2.82 (t, *J* = 7.6 Hz, 2 H), 1.57 (qu, *J* = 7.0 Hz, 2 H), 1.46 (s, 9 H), 1.28-1.15 (ovrlp, 12 H), 0.80 (t, *J* = 6.6 Hz, 3 H). **^{13}C NMR** (100 MHz,

$CDCl_3$): δ 175.4, 151.9, 124.1 (q, $^1J_{CF}$ = 278.4 Hz), 84.4, 44.2 (q, $^2J_{CF}$ = 34.8 Hz), 38.1, 32.0, 29.6, 29.5, 29.4, 29.2, 27.8, 25.1, 22.8, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.2. **HRMS** (ESI): Calcd for $C_{17}H_{30}F_3NO_3Na$ [M+Na]: 376.2076; Found: 376.2077. **IR** (neat, cm^{-1}): 1746, 1710, 1351, 1252, 1144, 1092, 628.

Synthesis of *tert*-Butyl Benzyl(6-chlorohexanoyl)carbamate (12).

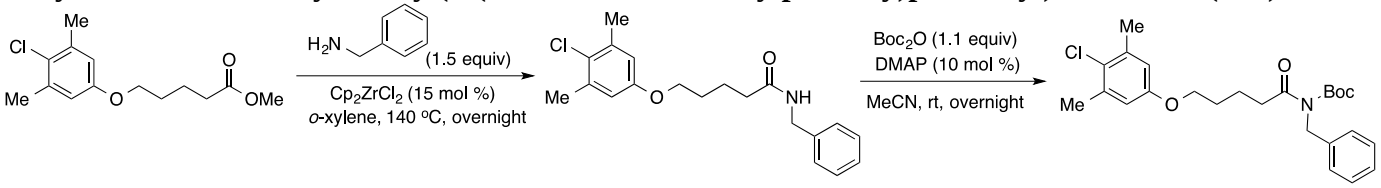


Step 1: An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with dimethylformamide solvent (DMF, 250 mL), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC.HCl, 1.1 equiv, 14.3 mmol, 2.78 g), 1-hydroxybenzotriazole hydrate (HOBt.H_2O, 1.1 equiv, 14.3 mmol, 2.18 g), triethylamine (Et_3N, 1.1 equiv, 14.3 mmol, 2.0 mL), benzylamine (1 equiv, 13 mmol, 1.39 g), and 6-chlorohexanoic acid (1 equiv, 13 mmol, 1.96 g). The reaction mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was washed with water (~500 mL) and ethyl acetate (EtOAc, ~100 mL). The organic fraction was further washed with dilute HCl solution (~1 M, ~100 mL), followed by saturated NaOH solution (~30 mL), and finally saturated NaCl solution (~50 mL). The organic fraction was dried with $MgSO_4$ powder and then dried *in vacuo* with the aid of a rotary evaporator to obtain the residue as a secondary amide, *N*-benzyl-6-chlorohexanamide.

Step 2: All *N*-benzyl-6-chlorohexanamide prepared from step 1 was transferred into an oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, and acetonitrile solvent (MeCN, 100 mL), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 10 mol %, 158 mg), and di-*tert*-butyl dicarbonate (Boc_2O, 1.1 equiv, 3.l mL) were then added. The resulting mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was concentrated *in vacuo*, and the crude product was washed with EtOAc, ~100 mL) and dilute HCl solution (~1 M, ~100 mL). The organic fraction was further washed with saturated $NaHCO_3$ solution (~50 mL) followed by saturated NaCl solution (~100 mL). The organic fraction was dried and concentrated *in vacuo*, and the residue was purified by flash chromatography with silica gel (without prior washing with Et_3N/hexanes) using a mixture of hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale-yellow liquid (1.74 g, 39%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.36-7.24 (ovrlp, 5 H), 4.92 (s, 2 H), 3.57 (t, *J* = 5.2 Hz, 2 H), 2.96 (t, *J* = 5.4 Hz, 2 H), 1.83 (qu, *J* = 5.5 Hz, 2 H), 1.72 (qu, *J* = 6.2 Hz, 2 H), 1.56-1.50 ((m, 2 H), 1.45 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 176.0, 153.5, 139.1, 128.7, 127.8, 127.4, 83.4, 47.7, 45.4, 38.5, 32.9, 28.1, 26.9, 24.9. **HRMS** (ESI): Calcd for $C_{18}H_{26}ClNO_3Na$ [M+Na]: 362.1499; Found: 362.1508. **IR** (neat, cm^{-1}): 1731, 1693, 1368, 1144, 700.

Synthesis of *tert*-Butyl Benzyl(5-(4-chloro-3,5-dimethylphenoxy)pentanoyl)carbamate (S13).

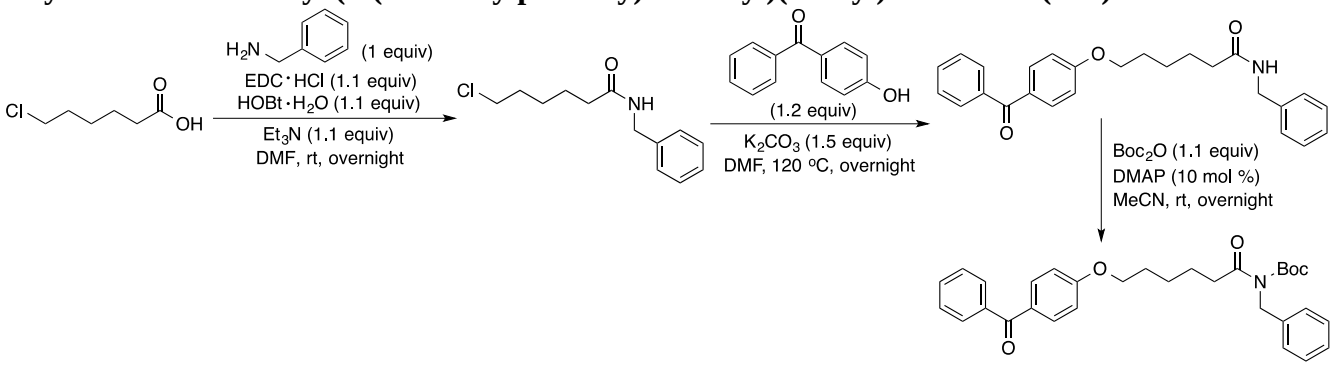


Step 1: In a nitrogen-filled glovebox, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with methyl 5-(4-chloro-3,5-dimethylphenoxy)pentanoate[8] (1 equiv, 3.25 mmol, 880 mg), benzylamine (1.5 equiv, 4.89 mmol, 0.60 mL), zirconocene dichloride (15 mol %, 142 mg), and *o*-xylene solvent (12 mL).The reaction mixture was then stirred at 140 ^{o}C in a preheated oil bath overnight. After the reaction, the reaction mixture was dried *in vacuo* with the aid of a rotary evaporator, and the residue was washed with dilute HCl solution (~1 M, ~100 mL) and ethyl acetate (EtOAc, ~50 mL). The organic fraction was further washed with saturated NaOH solution (~20 mL), and finally saturated NaCl solution (~50 mL). The organic fraction was dried with $MgSO_4$ powder and then concentrated *in vacuo* to obtain the residue as a secondary amide, *N*-benzyl-5-(4-chloro-3,5-dimethylphenoxy)pentanamide.

Step 2: All *N*-benzyl-5-(4-chloro-3,5-dimethylphenoxy)pentanamide prepared from step 1 was transferred into an oven-dried 250 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, and acetonitrile solvent (MeCN, 60 mL), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 10 mol %, 40 mg), and di-*tert*-butyl dicarbonate (Boc_2O, 1.3 equiv, 0.92 mL) were then added. The resulting mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was dried *in vacuo*, and the crude product was washed with EtOAc, ~100 mL) and dilute HCl solution (~1 M, ~100 mL). The organic fraction was further washed with saturated $NaHCO_3$ solution (~50 mL) followed by saturated NaCl solution (~100 mL). The organic fraction was then concentrated *in vacuo*, and the residue was purified by flash chromatography with silica gel (without prior washing with Et_3N/hexanes) using a mixture of hexanes/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (716 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.20 (ovrlp, 5 H), 6.62 (s, 2 H), 4.88 (s, 2 H), 3.92 (t. *J* = 5.8 Hz, 2 H), 2.99 (t. *J* = 7.2 Hz, 2 H), 2.32 (s, 6 H), 1.89-1.76 (ovrlp, 4 H), 1.40 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.9, 156.9, 153.2, 138.4, 137.0, 128.4, 127.6, 127.2, 126.1, 114.6, 83.2, 67.9, 47.4, 38.0, 28.8, 28.0, 21.9, 21.0. **HRMS** (ESI): Calcd for $C_{25}H_{32}ClNO_4Na$ [M+Na]: 468.1917; Found: 468.1896. **IR** (neat, cm^{-1}): 1732, 1693, 1371, 1323, 1149, 991, 861, 695. Mp: 50-52 ^{o}C.

Synthesis of *tert*-Butyl (6-(4-Benzoylphenoxy)hexanoyl)(benzyl)carbamate (S14).



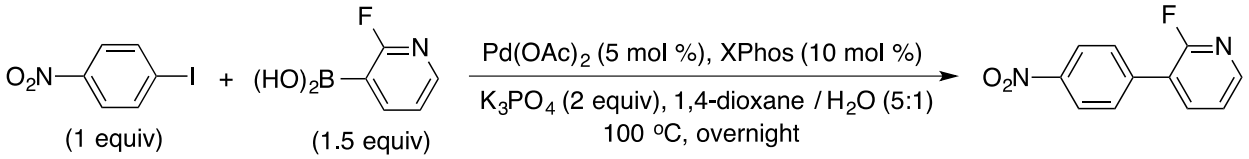
Step 1: An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with dimethylformamide solvent (DMF, 250 mL), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC.HCl, 1.1 equiv, 28.6 mmol, 5.6 g), 1-hydroxybenzotriazole hydrate (HOBt.H_2O, 1.1 equiv, 28.6 mmol, 4.4 g), triethylamine (Et_3N, 1.1 equiv, 28.6 mmol, 3.9 mL), benzylamine (1 equiv, 26 mmol, 2.8 g), and 6-chlorohexanoic acid (1 equiv, 26 mmol, 3.9 g). The reaction mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was washed with water (~500 mL) and ethyl acetate (EtOAc, ~100 mL). The organic fraction was further washed with dilute HCl solution (~1 M, ~100 mL), followed by saturated NaOH solution (~30 mL), and finally saturated NaCl solution (~50 mL). The organic fraction was dried with $MgSO_4$ powder and then dried *in vacuo* with the aid of a rotary evaporator to obtain the residue as *N*-benzyl-6-chlorohexanamide (61%, 22.1 mmol, 3.82 g).

Step 2: *N*-Benzyl-6-chlorohexanamide (1 equiv, 6 mmol, 1.44 g) prepared from step 1 was transferred into an oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, and 4-hydroxybenzophenone (1.1 equiv, 6.6 mmol, 1.31 g), K_2CO_3 (1.5 equiv, 9 mmol, 1.24 g), and DMF solvent (100 mL) were then added. The reaction was then heated at 120 ^oC in a preheated oil bath overnight. After the reaction, the reaction mixture was washed with water (~500 mL) and ethyl acetate (EtOAc, ~100 mL). The organic fraction was further washed with saturated NaOH solution (~100 mL x 2) followed by saturated NaCl solution (~100 mL). The organic fraction was concentrated *in vacuo*, and the residue was purified by flash chromatography with silica gel (without prior washing with Et_3N/hexanes) using a mixture of hexanes/EtOAc (5:1) as an eluent to afford 6-(4-benzoylphenoxy)-*N*-benzylhexanamide.

Step 3: All 6-(4-benzoylphenoxy)-*N*-benzylhexanamide prepared from step 2 was transferred into an oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, and acetonitrile solvent (MeCN, 100 mL), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 10 mol %, 73 mg), and di-*tert*-butyl dicarbonate (Boc_2O, 1.1 equiv, 1.44 mL) were then added. The resulting mixture was stirred at room temperature overnight. After the reaction, the reaction mixture was concentrated *in vacuo*, and the crude product was washed with EtOAc, ~100 mL) and dilute HCl solution (~1 M, ~100 mL). The organic fraction was further washed with saturated $NaHCO_3$ solution (~50 mL) followed by saturated NaCl solution (~100 mL). The organic fraction was dried and concentrated *in vacuo*, and the residue was purified by flash chromatography with silica gel (without prior washing with Et_3N/hexanes) using a mixture of hexanes/EtOAc (6:1) as an eluent to afford the title compound as a pale-yellow amorphous solid (2.15 g, 72%, yield based on 6-(4-benzoylphenoxy)-*N*-benzylhexanamide, prepared from Step 2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.7 Hz, 2 H), 7.74 (d, *J* = 7.2 Hz, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.3 Hz, 2 H), 7.30-7.18 (ovrlp, 5 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 4.89 (s, 2 H), 4.01 (t, *J* = 6.4 Hz, 2 H), 2.96 (t, *J* = 7.4 Hz, 2 H), 1.87-1.72 (ovrlp, 4 H), 1.53 (qu, *J* = 7.3 Hz, 2 H), 1.40 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.3, 175.8, 162.7, 153.0, 138.3, 132.4, 131.7, 129.8, 129.6, 128.2, 128.1, 127.4, 127.0, 114.0, 83.0, 67.9, 47.2, 38.1, 28.9, 27.8, 25.5, 24.8. **HRMS** (ESI): Calcd for $C_{31}H_{35}NO_5Na$ [M+Na]: 524.2413; Found: 524.2416. **IR** (neat, cm^{-1}): 1718, 1694, 1649, 1600, 1366, 1255, 1147, 995, 838, 740, 697. Mp: 61-63 ^oC.

Synthesis of 2-Fluoro-3-(4-nitrophenyl)pyridine (S15).

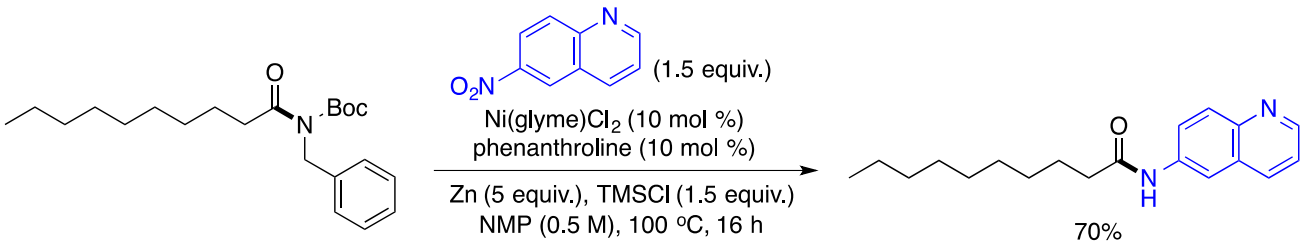


In a nitrogen-filled glovebox, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with 1-iodo-4-nitrobenzene (1 equiv, 4 mmol, 996 mg), (2-fluoropyridin-3-yl)boronic acid (1.5 equiv, 6 mmol, 846 mg), $Pd(OAc)_2$ (5 mol %, 45 mg), XPhos (10 mol%, 191 mg), K_3PO_4 (2 equiv, 8 mmol, 1.70 g), 1,4-dioxane solvent (10 mL), and deionized water (2 mL). The reaction mixture was then stirred at 100 ^oC in a preheated oil bath overnight. After the reaction, the reaction mixture was washed with water (~100 mL) and ethyl acetate (EtOAc, ~50 mL). The aqueous fraction was further washed with EtOAc (2 x 20 mL). The combined organic fraction was dried with $MgSO_4$ powder and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash chromatography with silica gel (without prior washing with Et_3N/hexanes) using a mixture of hexanes/EtOAc (5:1) as an eluent to afford the title compound as an off-white solid (572 mg, 66%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.34 (d, J = 8.9 Hz, 2 H), 8.32-8.30 (m, 1 H), 7.96-7.91 (m, 1 H), 7.76 (dd, J_{HH} = 8.8 Hz, J_{HF} = 1.5 Hz, 2 H),7.38-7.35 (m, 1 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 160.3 (d, J_{CF} = 239.6 Hz), 148.2 (d, J_{CF} = 14.9 Hz), 147.9, 140.9 (d, J_{CF} = 3.7 Hz), 140.8 (d, J_{CF} = 5.2 Hz), 129.9 (d, J_{CF} = 3.3 Hz), 124.1, 122.3 (d, J_{CF} = 4.5 Hz), 121.9 (d, J_{CF} = 27.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.2. **HRMS** (ESI): Calcd for $C_{11}H_8FN_2O_2$ [M+H]: 219.0564; Found: 219.0560. **IR** (neat, cm^{-1}): 1607, 1512, 1447, 1398, 1345, 856, 842, 799, 762, 734, 693. Mp: 183-185 ^oC.

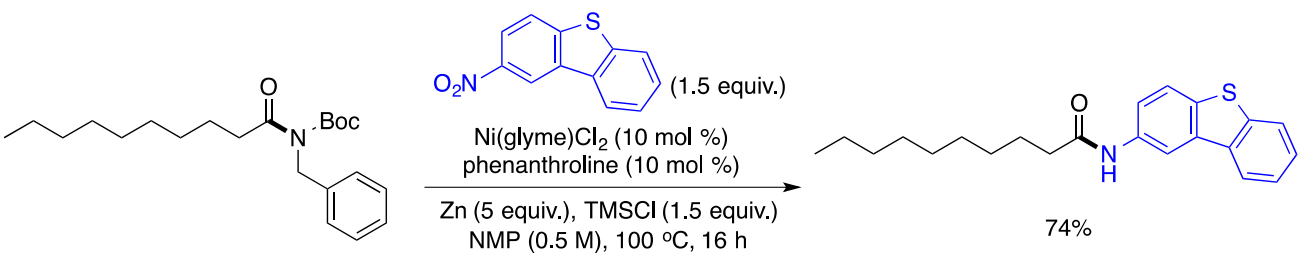
Synthesis of Amides via Nickel-Catalyzed Reductive Transamidation of Boc-activated Secondary Amides with Nitroarenes

Nickel-Catalyzed Reductive Transamidation of Boc-activated Secondary Alkyl Amide with Nitroarene (General Procedure B). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with zinc powder (Zn, 5 equiv.), Boc-activated amide (1 equiv.), nitroarene (1.5 equiv.), 1,10-phenanthroline (phen, 10-20 mol %), nickel(II) chloride ethylene glycol dimethyl ether complex ($Ni(glyme)Cl_2$, 10-20 mol %), *N*-methylpyrrolidone solvent (NMP, 0.5 M with respect to amide), and chlorotrimethylsilane (TMSCl, 1-1.5 equiv). The resulting mixture was stirred at a preheated oil bath for 16 h. After the reaction, the reaction mixture was cooled down to room temperature, and it was acidified with saturated NH_4Cl solution (~5 mL) and then neutralized with saturated $NaHCO_3$ solution (~10 mL). The crude product in the aqueous fraction was extracted with ethyl acetate (EtOAc, ~20 mL). The aqueous fraction was further washed with EtOAc (3 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by preparative thin-layer chromatography (TLC) using a solvent mixture (hexanes and EtOAc) as an eluent to afford the purified amide product.

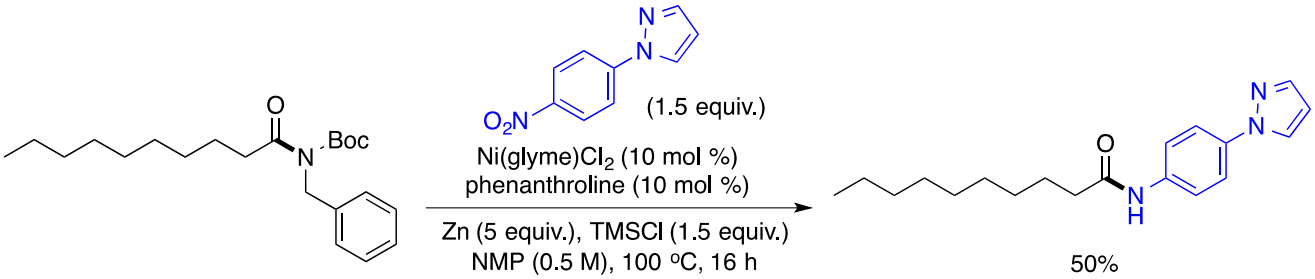
Nickel-Catalyzed Reductive Transamidation of Boc-activated Secondary Aryl Amide with Nitroarene (General Procedure C). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with manganese powder (Mn, 5 equiv.), Boc-activated amide (1 equiv.), nitroarene (1.5 equiv.), 2,2′:6′,2″-terpyridine (terpyridine, 7.5-20 mol %), nickel(II) chloride ethylene glycol dimethyl ether complex (Ni(glyme)Cl_2, 7.5-20 mol %), *N*-methylpyrrolidone solvent (NMP, 0.5 M with respect to amide), and iodotrimethylsilane (TMSI, 1-2 equiv). The resulting mixture was stirred at a preheated oil bath for 16 h. After the reaction, the reaction mixture was cooled down to room temperature, and it was acidified with saturated NH_4Cl solution (~5 mL) and then neutralized with saturated $NaHCO_3$ solution (~10 mL). The crude product in the aqueous fraction was extracted with ethyl acetate (EtOAc, ~20 mL). The aqueous fraction was further washed with EtOAc (3 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by preparative thin-layer chromatography (TLC) using a solvent mixture (hexanes and EtOAc) as an eluent to afford the purified amide product.



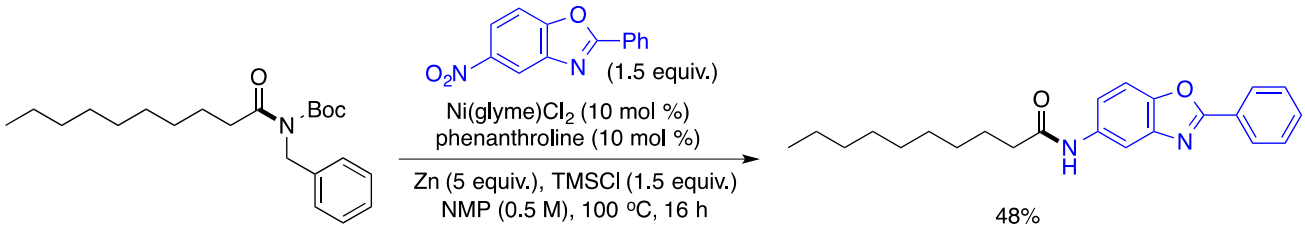
***N*-(Quinolin-6-yl)decanamide (3a).**[8] Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(decanoyl)carbamate (1 equiv, 0.50 mmol, 181 mg), 6-nitroquinoline (1.5 equiv, 0.75 mmol, 131 mg), Ni(glyme)Cl_2 (10 mol %, 11.0 mg), phen (10 mol %, 9.0 mg), Zn (5 equiv, 2.5 mmol, 164 mg), TMSCl (1.5 equiv, 0.75 mmol, 96 μL), and NMP (1.0 mL) at the reaction temperature of 100 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (2:1) as an eluent to afford the title compound as a pale brown amorphous solid (105 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 8.70 (s, 1 H), 8.45 (s, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 7.98 (d, J = 9.0 Hz, 1 H), 7.61 (d, J = 9.1 Hz, 1 H), 7.34 (dd, J = 8.4 Hz, J = 4.3 Hz, 1 H), 2.42 (t, J = 7.6 Hz, 2 H), 1.74 (qu, J = 7.7 Hz, 2 H), 1.36-1.17 (ovrlp, 12 H), 0.86 (t, J = 7.1 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.5, 149.2 145.4, 136.5, 136.1, 129.8, 129.0, 123.5, 121.7, 116.2, 37.8, 31.9, 29.50, 29.47, 29.39, 29.3, 25.8, 22.7, 14.2. . **IR** (neat, cm^{-1}): 3282, 1682, 1664, 1542, 1466, 1381, 1234, 834.



***N*-(Dibenzo[*b*,*d*]thiophen-3-yl)decanamide (3b).** Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(decanoyl)carbamate (0.50 mmol, 181 mg), 3-nitrodibenzo[*b*,*d*]thiophene (0.75 mmol, 172 mg), Ni(glyme)Cl_2 (10 mol %, 11.0 mg), phen (10 mol %, 9.0 mg), Zn (5 equiv, 2.5 mmol, 164 mg), TMSCl (1.5 equiv, 0.75 mmol, 96 μL), and NMP (1.0 mL) at the reaction temperature of 100 ^{o}C.. The crude product was purified by preparative TLC using hexanes/EtOAc (8:1) as an eluent to afford the title compound as a brown amorphous solid (130 mg, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1 H), 8.00 (d, *J* = 7.7 Hz, 1 H), 7.81-7.76 (ovrlp, 2 H), 7.66 (d, *J* = 8.5 Hz, 1 H), 7.42-7.32 (ovrlp, 3 H), 2.37 (t, *J* = 7.7 Hz, 2 H), 1.73 (qu, *J* = 7.0 Hz, 2 H), 1.36-1.19 (ovrlp, 12 H), 0.87 (t, *J* = 6.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.1, 140.2, 136.2, 135.4, 135.2, 134.9, 126.9, 124.4, 122.95, 122.85, 121.9, 119.8, 113.2, 37.9, 32.0, 29.59, 29.55, 29.5, 29.4, 25.8, 22.8, 14.2. **HRMS** (ESI): Calcd for $C_{22}H_{28}NO_S$ [M+H]: 354.1900; Found: 354.1885. **IR** (neat, cm^{-1}): 3284, 1652, 1572, 1520, 1469, 1413, 1223, 808, 756, 725. Mp: 136-138 ^{o}C.

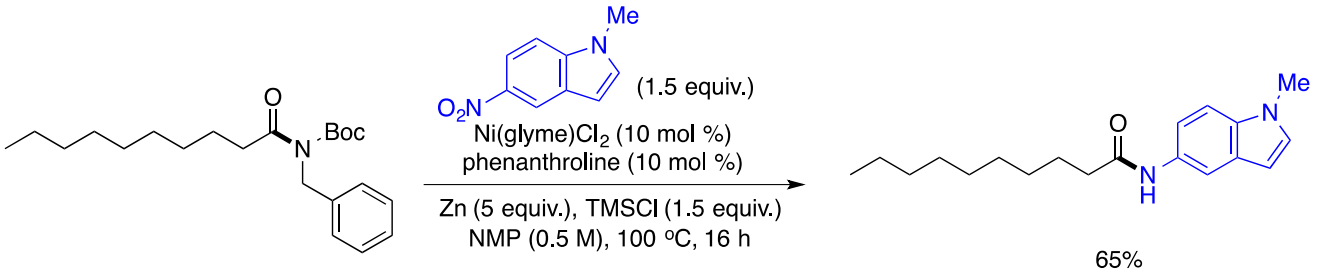


***N*-(4-(1*H*-Pyrazol-1-yl)phenyl)decanamide (3c).**[8] Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(decanoyl)carbamate (1 equiv, 0.50 mmol, 181 mg), 1-(4-nitrophenyl)-1*H*-pyrazole (1.5 equiv, 0.75 mmol, 142 mg), Ni(glyme)Cl_2 (10 mol %, 11.0 mg), phen (10 mol %, 9.0 mg), Zn (5 equiv, 2.5 mmol, 164 mg), TMSCl (1.5 equiv, 0.75 mmol, 96 μL), and NMP (1.0 mL) at the reaction temperature of 100 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (4:1) as an eluent to afford the title compound as an off-white amorphous solid (78 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H), 7.70 (s, 1 H), 7.65-7.56 (ovrlp, 4 H), 7.47 (s, 1 H), 6.45 (s, 1 H), 2.36 (t, *J* = 7.6 Hz, 2 H), 1.72 (qu, *J* = 7.6 Hz, 2 H), 1.41-1.20 (ovrlp, 12 H), 0.88 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 141.0, 136.6, 136.5, 126.9, 120.7, 120.0, 107.6, 37.9, 32.0, 29.6, 29.5, 29.43, 29.41, 25.7, 22.8, 14.2. **IR** (neat, cm^{-1}): 3326, 1659, 1524, 1392, 1307, 1049, 937, 818.



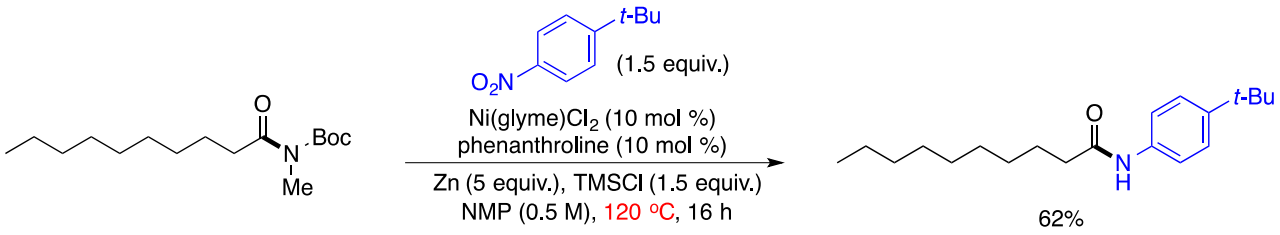
***N*-(2-Phenylbenzo[*d*]oxazol-5-yl)decanamide (3d).**[8] Following the general procedure B, the title

compound was prepared using *tert*-butyl benzyl(decanoyl)carbamate (1 equiv, 0.50 mmol, 181 mg), 5-nitro-2-phenylbenzo[*d*]oxazole (1.5 equiv, 0.75 mmol, 180 mg), Ni(glyme)Cl_2 (10 mol %, 11.0 mg), phen (10 mol %, 9.0 mg), Zn (5 equiv, 2.5 mmol, 164 mg), TMSCl (1.5 equiv, 0.75 mmol, 96 μL), and NMP (1.0 mL) at the reaction temperature of 100 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (8:1) as an eluent to afford the title compound as a pale brown amorphous solid (87 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 6.8 Hz, 2 H), 7.90 (s, 1 H), 7.77 (s, 1 H), 7.56-7.45 (ovrlp, 5 H), 2.36 (t, *J* = 7.6 Hz, 2 H), 1.72 (qu, *J* = 7.5 Hz, 2 H), 1.36-1.24 (ovrlp, 12 H), 0.86 (d, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.9, 163.9, 147.6, 142.5, 135.2, 131.7, 129.0, 127.7, 127.1, 118.5, 111.7, 110.5, 37.8, 32.0, 29.6, 29.53, 29.46, 29.4, 25.8, 22.8, 14.2. **IR** (neat, cm^{-1}): 3288, 1650, 1552, 1469, 1193, 1056, 775, 701.



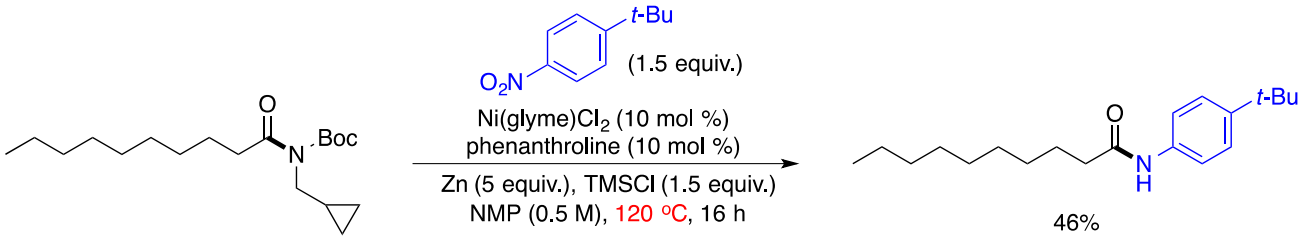
***N*-(1-Methyl-1*H*-indol-5-yl)decanamide (3e).**[8] Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(decanoyl)carbamate (0.35 mmol, 127 mg), 1-methyl-5-nitro-1*H*-indole (0.525 mmol, 93 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 100 °C. The crude product was purified by preparative TLC using hexanes/CH_2Cl_2 (8:1) as an eluent to afford the title compound as a deep brown amorphous solid (68 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (s, 1 H), 7.28-7.24 (ovrlp, 2 H), 7.21 (s, 1 H), 7.03 (d, *J* = 3.1 Hz, 1 H), 6.42 (d, *J* = 3.1 Hz, 1 H), 3.76 (s, 3 H), 2.35 (t, *J* = 7.6 Hz, 2 H), 1.74 (qu, *J* = 7.6 Hz, 2 H), 1.39-1.19 (ovrlp, 12 H), 0.88 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.5, 134.3, 130.3, 129.7, 128.6, 116.0, 112.9, 109.4, 101.1, 38.0, 33.1, 32.0, 29.62. 29.57, 29.5, 29.4, 26.0, 22.8, 14.3. **IR** (neat, cm^{-1}): 3289, 1652, 1539, 1302, 1244, 799, 711.

***N*-(4-(*tert*-Butyl)phenyl)decanamide (3f).**[8]

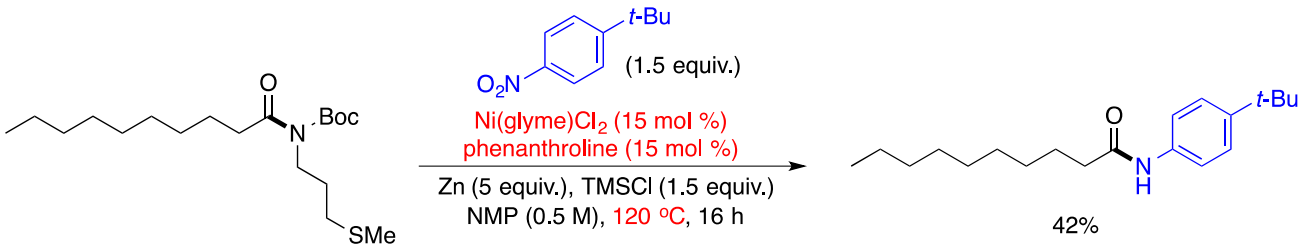


(i) From *tert*-Butyl Decanoyl(methyl)carbamate (P-2, Figure 3 in maintext). Following the general procedure B, the title compound was prepared using *tert*-butyl decanoyl(methyl)carbamate

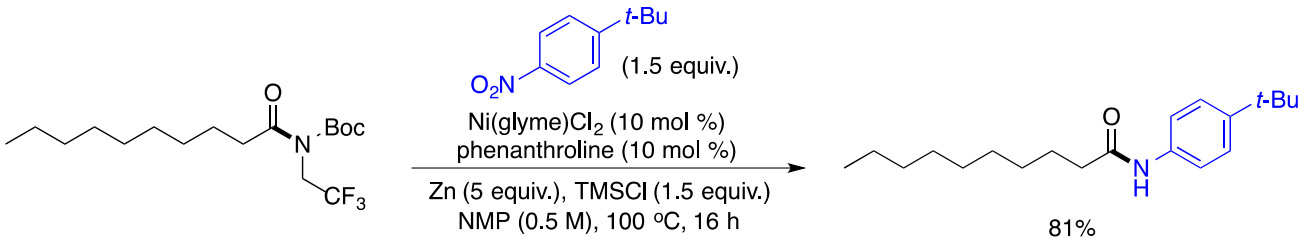
(0.35 mmol, 100 mg), 1-(*tert*-butyl)-4-nitrobenzene (0.525 mmol, 94 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 120 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a brown amorphous solid (66 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.5 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.27 (s, 1 H), 2.33 (t, *J* = 7.6 Hz, 2 H), 1.72 (qu, *J* = 7.3 Hz, 2 H), 1.39-1.22 (ovrlp, 21 H), 0.88 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.5, 147.2, 135.5, 125.9, 119.8, 37.9, 34.5, 32.0, 31.5, 29.6, 29.5, 29.4, 25.9, 22.8, 14.2. **IR** (neat, cm^{-1}): 3301, 1659, 1604, 1538, 1315, 833, 728.



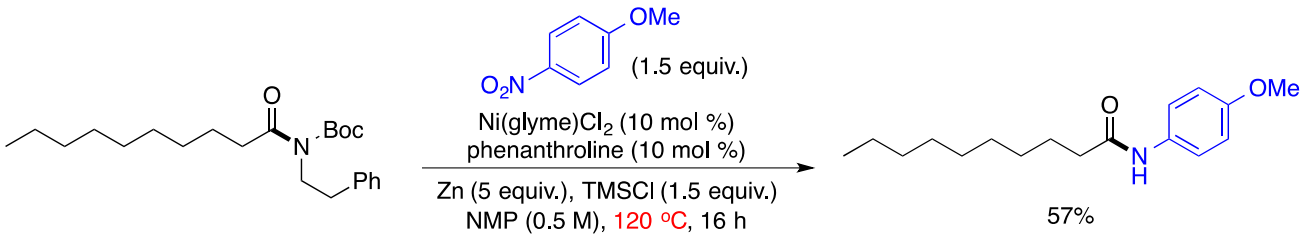
(ii) From *tert*-Butyl (Cyclopropylmethyl)(decanoyl)carbamate (P-4, Figure 3 in maintext). Following the general procedure B, the title compound was prepared using *tert*-butyl (cyclopropylmethyl)(decanoyl)carbamate (0.35 mmol, 114 mg), 1-(*tert*-butyl)-4-nitrobenzene (0.525 mmol, 94 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 120 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a brown amorphous solid (49 mg, 46%). Spectral and analytical data were identical to those reported for the same compound above.



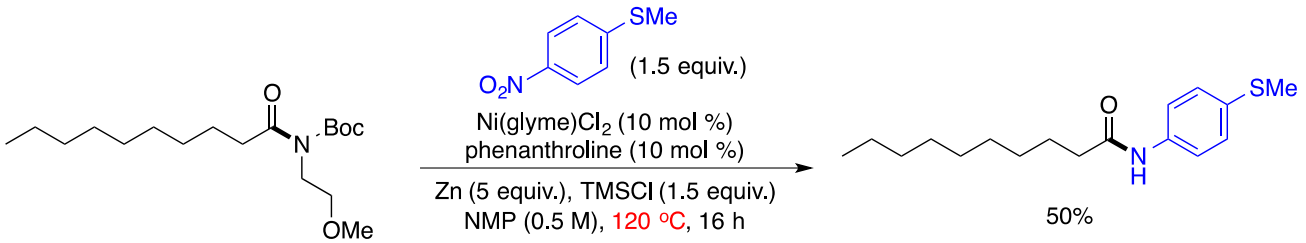
(iii) From *tert*-Butyl Decanoyl(3-(methylthio)propyl)carbamate (P-6, Figure 3 in maintext). Following the general procedure B, the title compound was prepared using *tert*-butyl (cyclopropylmethyl)(decanoyl)carbamate (0.35 mmol, 126 mg), 1-(*tert*-butyl)-4-nitrobenzene (0.525 mmol, 94 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), phen (15 mol %, 9.5 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 120 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a brown amorphous solid (45 mg, 42%). Spectral and analytical data were identical to those reported for the same compound above.



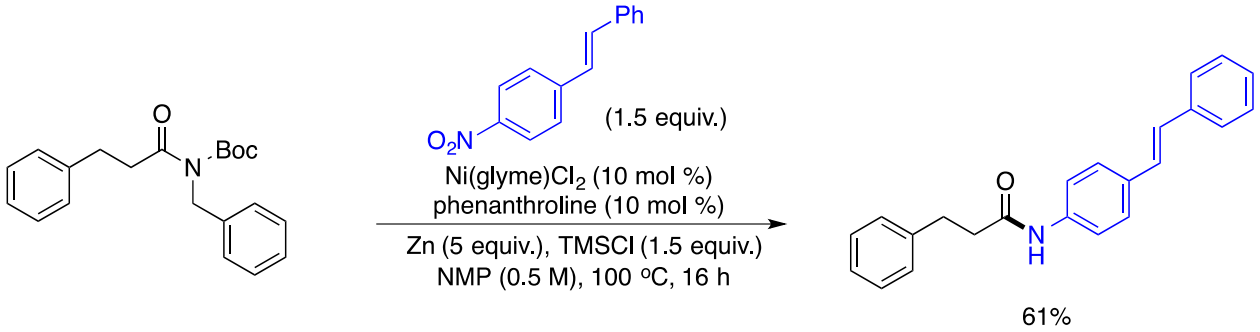
(iv) From *tert*-Butyl Decanoyl(2,2,2-trifluoroethyl)carbamate (P-7, Figure 3 in maintext). Following the general procedure B, the title compound was prepared using *tert*-butyl decanoyl(2,2,2-trifluoroethyl)carbamate (0.35 mmol, 124 mg), 1-(*tert*-butyl)-4-nitrobenzene (0.525 mmol, 94 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 100 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a brown amorphous solid (84 mg, 81%). Spectral and analytical data were identical to those reported for the same compound above.



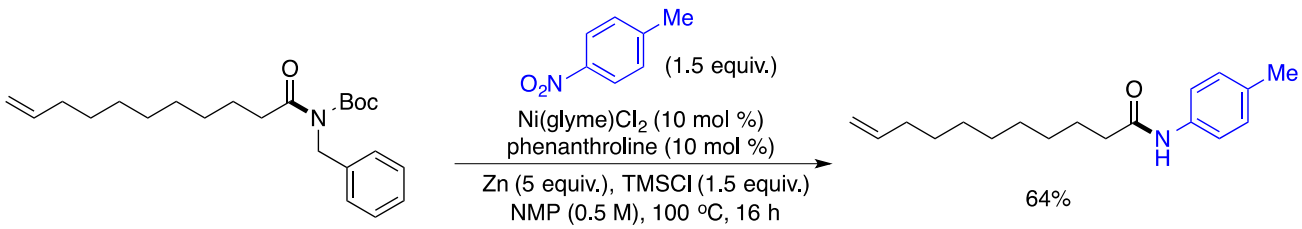
***N*-(4-methoxyphenyl)decanamide (3g).**[8] Following the general procedure B, the title compound was prepared using *tert*-butyl decanoyl(phenethyl)carbamate (0.35 mmol, 132 mg), 4-nitroanisole (0.525 mmol, 80 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 120 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a brown amorphous solid (55 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.8 Hz, 2 H), 7.15 (s, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 3.78 (s, 3 H), 2.32 (t, *J* = 7.6 Hz, 2 H), 1.71 (qu, *J* = 7.3 Hz, 2 H), 1.39-1.21 (ovrlp, 12 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.4, 156.5, 131.2, 121.9, 114.2, 55.6, 37.8, 32.0, 29.6, 29.5, 29.45, 29.42, 25.9, 22.8, 14.2.



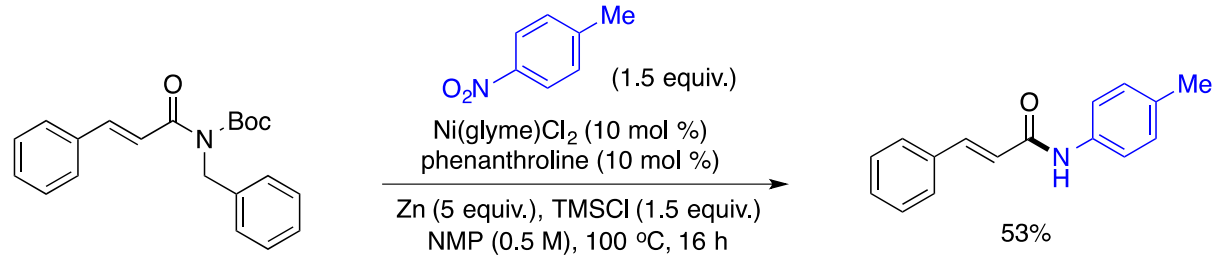
***N*-(4-(methylthio)phenyl)decanamide (3h).**[8] Following the general procedure B, the title compound was prepared using *tert*-butyl decanoyl(2-methoxyethyl)carbamate (0.35 mmol, 132 mg), 4-nitrothioanisole (0.525 mmol, 89 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 120 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (7:1) as an eluent to afford the title compound as a brown amorphous solid (52 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2 H), 7.23 (d, *J* = 8.6 Hz, 2 H), 7.12 (s, 1 H), 2.46 (s, 3 H), 2.34 (t, *J* = 7.6 Hz, 2 H), 1.72 (qu, *J* = 7.3 Hz, 2 H), 1.38-1.23 (ovrlp, 12 H), 0.88 (d, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.4, 135.8, 133.5, 128.2, 120.5, 38.0, 32.0, 29.6, 29.5, 29.4, 25.8, 22.8, 16.9, 14.3. **HRMS** (ESI): Calcd for $C_{17}H_{28}NOS$ [M+H]: 294.1891; Found: 294.1892.



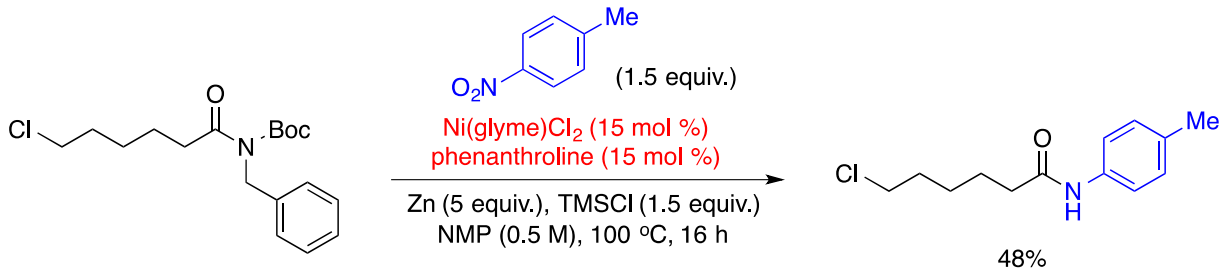
(*E*)-3-Phenyl-*N*-(4-styrylphenyl)propanamide (3i).[8] Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(3-phenylpropanoyl)carbamate (0.35 mmol, 119 mg), (*E*)-1-nitro-4-styrylbenzene (0.525 mmol, 118 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 100 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a pale brown amorphous solid (70 mg, 61%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.00 (s, 1 H), 7.62-7.52 (ovrlp, 6 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.31-7.23 (ovrlp, 5 H), 7.21-7.12 (ovrlp, 3 H), 2.92 (t, *J* = 7.8 Hz, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 170.4, 141.2, 138.8, 137.2, 131.9, 128.7, 128.34, 128.26, 128.04, 127.4, 126.93, 126.90, 126.3, 126.0, 119.1, 38.0, 30.8. **IR** (neat, cm^{-1}): 3278, 1648, 1593, 1515, 1412, 1075, 967, 819, 690.



***N*-(*p*-Tolyl)undec-10-enamide (3j).** Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(undec-10-enoyl)carbamate (0.30 mmol, 112 mg), 4-nitrotoluene (0.45 mmol, 62 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), phen (10 mol %, 5.4 mg), Zn (5 equiv, 1.5 mmol, 98 mg), TMSCl (1.5 equiv, 0.45 mmol, 57 μL), and NMP (0.6 mL) at the reaction temperature of 100 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale brown amorphous solid (53 mg, 64%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.43 (s, 1 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.11 (d, *J* = 8.2 Hz, 2 H), 5.88-5.78 (m, 1 H), 5.02-4.97 (m, 1 H), 4.94-4.91 (m, 1 H), 2.32-2.28 (ovrlp, 5 H), 2.04 (q, *J* = 7.3 Hz, 2 H), 1.68 (d, *J* = 6.4 Hz, 2 H), 1.40-1.27 (ovrlp, 10 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 171.7, 139.7, 136.2, 134.1, 129.7, 120.3, 114.3, 38.0, 34.2, 29.8, 29.7, 29.5, 29.4, 26.1, 21.0. **HRMS** (ESI): Calcd for $C_{18}H_{28}NO$ [M+H]: 274.2171; Found: 274.2190. **IR** (neat, cm^{-1}): 3303, 1660, 1594, 1523, 1404, 1251, 1180, 911, 814. Mp: 68-70 °C.

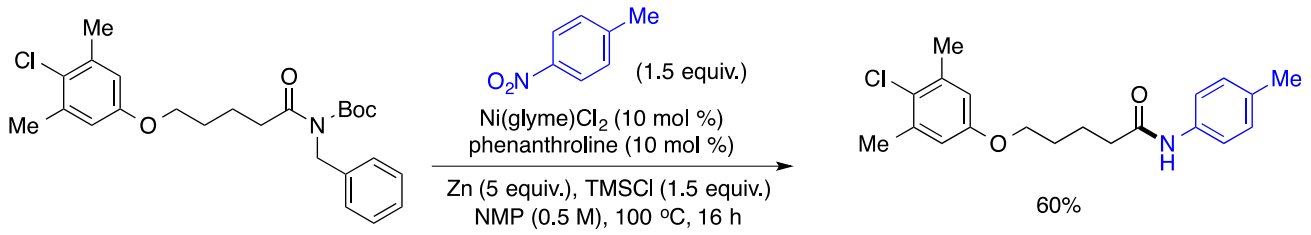


***N*-(*p*-Tolyl)cinnamamide (3k).**[8] Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(cinnamoyl)carbamate (0.30 mmol, 101 mg), 4-nitrotoluene (0.45 mmol, 62 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), phen (10 mol %, 5.4 mg), Zn (5 equiv, 1.5 mmol, 98 mg), TMSCl (1.5 equiv, 0.45 mmol, 57 μL), and NMP (0.6 mL) at the reaction temperature of 100 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (38 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 7.70 (d, *J* = 15.6 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 7.1 Hz, 2 H), 7.31-7.22 (ovrlp, 3 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 6.65 (d, *J* = 15.5 Hz, 1 H), 2.27 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.6, 142.0, 135.7, 134.8, 134.1, 129.8, 129.6, 128.8, 128.0, 121.4, 120.5, 21.0. **IR** (neat, cm^{-1}): 3256, 1659, 1621, 1598, 1540, 1347, 985, 813.

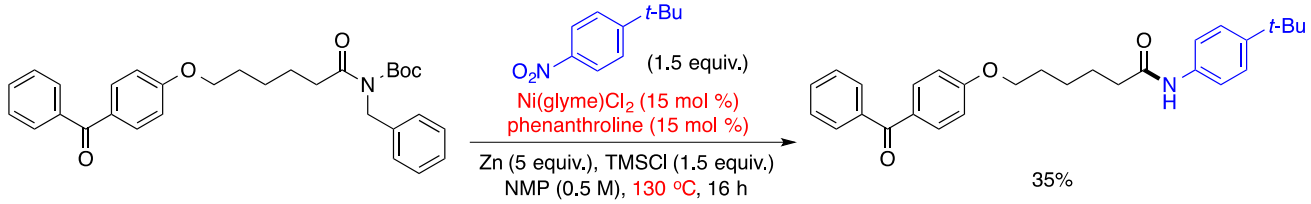


6-Chloro-*N*-(*p*-tolyl)hexanamide (3l). Following the general procedure B, the title compound was prepared using 6-chloro-*N*-(*p*-tolyl)hexanamide (1 equiv, 0.35 mmol, 119 mg), 4-nitrotoluene (1.5

equiv, 0.525 mmol, 94 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 100 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (40 mg, 48%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.38 (d, *J* = 8.1 Hz, 2 H), 7.24 (s, 1 H), 7.12 (d, *J* = 8.1 Hz, 2 H), 3.56 (t, *J* = 6.6 Hz, 2 H), 2.35-2.30 (ovrlp, 5 H), 1.81 (qu, *J* = 7.3 Hz, 2 H), 1.72 (qu, *J* = 7.5 Hz, 2 H), 1.50 (qu, *J* = 7.9 Hz, 2 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 171.1, 136.1, 134.2, 129.8, 120.3, 45.5, 37.7, 32.8, 26.9, 25.2, 21.0. **HRMS** (ESI): Calcd for $C_{13}H_{19}ClNO$ [M+H]: 240.1155; Found: 240,1167. **IR** (neat, cm^{-1}): 3320, 1654, 1594, 1526, 1403, 1307, 814, 646. Mp: 83-85 ^{o}C.

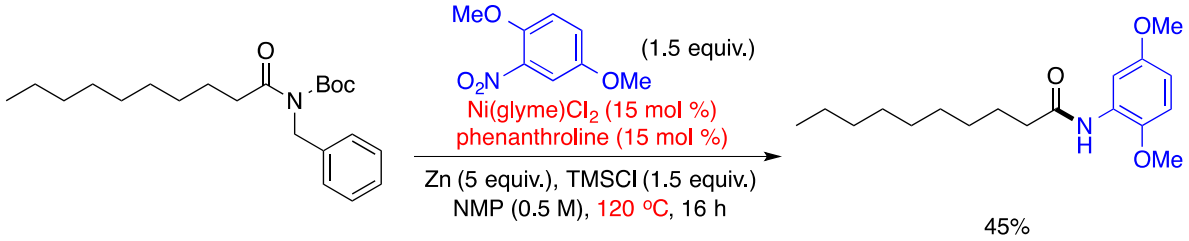


5-(4-Chloro-3,5-dimethylphenoxy)-*N*-(*p*-tolyl)pentanamide (3m).[21] Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(5-(4-chloro-3,5-dimethylphenoxy)pentanoyl)carbamate (1 equiv, 0.35 mmol, 156 mg), 4-nitrotoluene (1.5 equiv, 0.525 mmol, 72 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), phen (10 mol %, 6.3 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7 mL) at the reaction temperature of 100 ^{o}C. The crude product was purified by preparative TLC using hexanes/EtOAc (8:1) as an eluent to afford the title compound as an off-white amorphous solid (73 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.59 (s, 2 H), 3.89 (t, *J* = 5.7 Hz, 2 H), 2.38 (t, *J* = 6.8 Hz, 2 H), 2.31 (s, 6 H), 2.28 (s, 3 H), 1.89-1.77 (ovrlp, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 156.8, 137.1, 135.5, 133.9, 129.5, 126.2, 120.2, 114.5, 67.7, 37.1, 28.7, 22.5, 21.0, 20.9. **IR** (neat, cm^{-1}): 3276, 1634, 1595, 1540, 1466, 1323, 1166, 1044, 819, 699, 669.

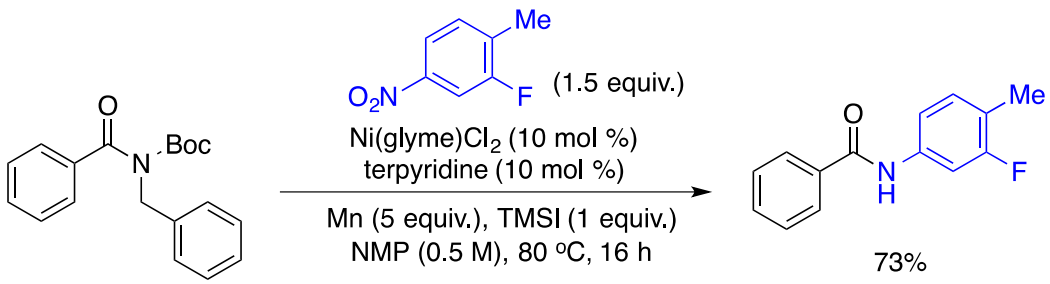


6-(4-Benzoylphenoxy)-*N*-(4-(*tert*-butyl)phenyl)hexanamide (3n). Following the general procedure B, the title compound was prepared using *tert*-butyl (6-(4-benzoylphenoxy)hexanoyl)(benzyl)carbamate (1 equiv, 0.35 mmol, 176 mg), 1-(*tert*-butyl)-4-nitrotoluene (1.5 equiv, 0.525 mmol, 94 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), phen (15 mol %, 9.5 mg), Zn (5 equiv, 1.75 mmol, 114.5 mg), TMSCl (1.5 equiv, 0.525 mmol, 67 μL), and NMP (0.7

mL) at the reaction temperature of 130 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (5:1) as an eluent to afford the title compound as an off-white amorphous solid (55 mg, 35%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.49-7.42 (ovrlp, 4 H), 7.34-7.29 (ovrlp, 3 H), 6.93 (d, *J* = 8.1 Hz, 2 H), 4.04 (d, *J* = 6.1 Hz, 2 H), 2.39 (t, *J* = 7.2 Hz, 2 H), 1.89-1.78 (ovrlp, 4 H), 1.57 (qu, *J* = 6.9 Hz, 2 H), 1.29 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.8, 171.1, 162.9, 147.4, 138.4, 135.4, 132.7, 132.0, 130.1, 129.9, 128.3, 125.9, 119.7, 114.1, 68.0, 37.6, 34.5, 31.5, 29.0, 25.8, 25.4. **HRMS** (ESI): Calcd for $C_{29}H_{33}NO_3Na$ [M+Na]: 466.2353; Found: 466.2345. **IR** (neat, cm^{-1}): 3361, 1675, 1635, 1598, 1527, 1253, 1021, 837, 739, 698. Mp: 121-123 °C.

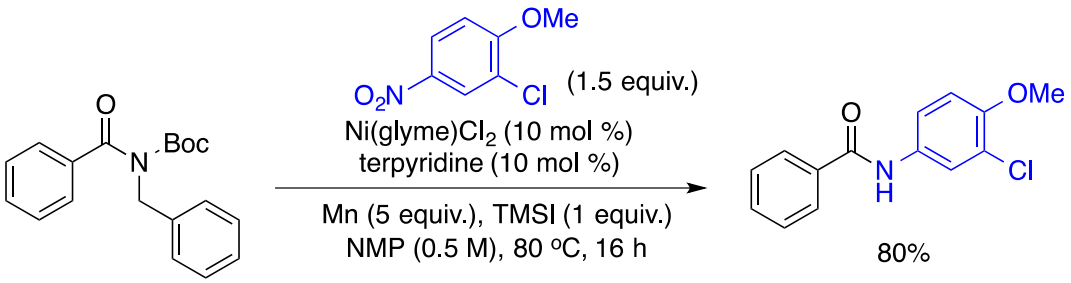


***N*-(2,5-dimethoxyphenyl)decanamide (3o).** Following the general procedure B, the title compound was prepared using *tert*-butyl benzyl(decanoyl)carbamate (1 equiv, 0.30 mmol, 108 mg), 2,5-dimethoxynitrotoluene (1.5 equiv, 0.45 mmol, 82 mg), Ni(glyme)Cl_2 (15 mol %, 9.9 mg), phen (15 mol %, 8.1 mg), Zn (5 equiv, 1.5 mmol, 98 mg), TMSCl (1.5 equiv, 0.45 mmol, 57 μL), and NMP (0.6 mL) at the reaction temperature of 120 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (42 mg, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 2.6 Hz, 1 H), 7.77 (s, 1 H), 6.78 (d, *J* = 8.9 Hz, 1 H), 6.56 (dd, *J* = 8.9 Hz, *J* = 3.0 Hz, 1 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 2.38 (t, *J* = 7.5 Hz, 2 H), 1.73 (qu, *J* = 7.6 Hz, 2 H), 1.41-1.26 (ovrlp, 12 H), 0.88 (d, *J* = 6.9 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.5, 154.0, 142.0, 128.6, 110.8, 108.6, 105.9, 56.3, 55.9, 38.3, 32.0, 29.6, 29.5, 29.42, 29.38, 25.7, 22.8, 14.2. **HRMS** (ESI): Calcd for $C_{18}H_{29}NO_3Na$ [M+Na]: 330.2045; Found: 330.2047. **IR** (neat, cm^{-1}): 3259, 1660, 1595, 1537, 1493, 1223, 1038, 803, 721. Mp: 65-67 °C.

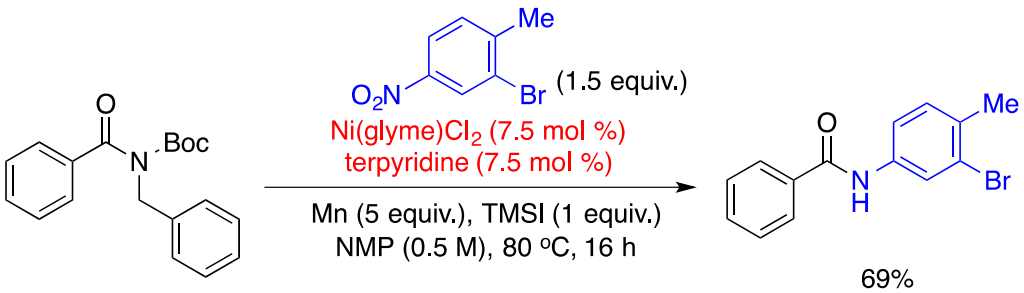


***N*-(3-Fluoro-4-methylphenyl)benzamide (4a).** Following the general procedure C, the title compound was prepared using *tert*-butyl benzoyl(benzyl)carbamate (0.30 mmol, 93 mg), 2-fluoro-4-nitrotoluene (0.45 mmol, 70 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), terpyridine (10 mol %, 7.0 mg),

Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 80 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (50 mg, 73%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.98 (s, 1 H), 7.85 (d, J = 7.4 Hz, 2 H), 7.59-7.55 (ovrlp, 2 H), 7.49 (t, J = 7.2 Hz, 2 H), 7.20-7.14 (ovrlp, 2 H), 2.25 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.9, 161.6 (d, $^1J_{CF}$ = 241.4 Hz), 137.8 (d, $^3J_{CF}$ = 10.7 Hz), 135.3, 132.3, 131.8 (d, $^3J_{CF}$ = 6.4 Hz), 129.2, 127.4, 121.1 (d, $^2J_{CF}$ = 17.4 Hz), 115.8 (d, $^4J_{CF}$ = 3.4 Hz), 107.8 (d, $^2J_{CF}$ = 27.3 Hz), 14.2 (d, $^3J_{CF}$ = 3.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -118.4. **HRMS** (ESI): Calcd for $C_{14}H_{13}FNO$ [M+H]: 230.0981; Found: 230.0984. **IR** (neat, cm^{-1}): 3319, 1653, 1597, 1508, 1413, 1267, 858, 813. Mp: 117-119 °C.

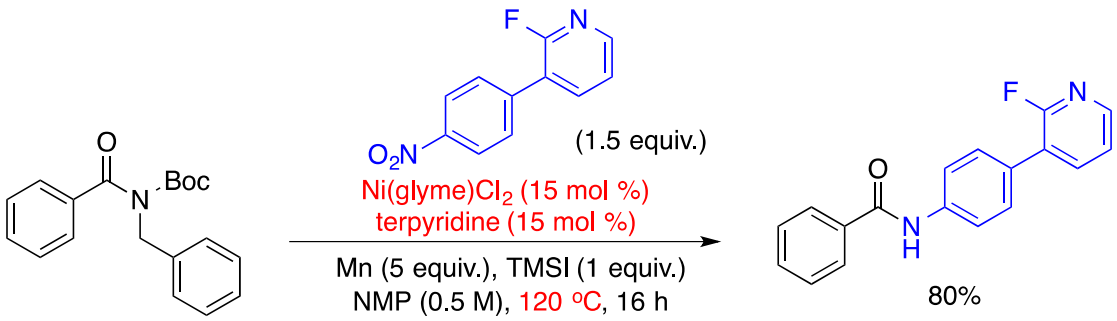


***N*-(3-Chloro-4-methoxyphenyl)benzamide (4b).** Following the general procedure C, the title compound was prepared using *tert*-butyl benzoyl(benzyl)carbamate (0.30 mmol, 93 mg), 2-chloro-4-nitroanisole (0.45 mmol, 84 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), terpyridine (10 mol %, 7.0 mg), Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 80 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (5:1) as an eluent to afford the title compound as an off-white amorphous solid (63 mg, 80%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.00 (s, 1 H), 7.84 (d, J = 7.0 Hz, 2 H), 7.73 (s, 1 H), 7.55 (d, J = 6.9 Hz, 1 H), 7.50-7.44 (ovrlp, 3 H), 6.92 (d, J = 8.8 Hz, 1 H), 3.88 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 166.0, 152.5, 135.1, 132.2, 132.1, 129.1, 127.4, 123.2, 122.7, 120.6, 112.7, 56.7. **HRMS** (ESI): Calcd for $C_{14}H_{13}ClNO_2$ [M+H]: 262.0645; Found: 262.0641. **IR** (neat, cm^{-1}): 3303, 1648, 1515, 1500, 1403, 1253, 1219, 1059, 1019, 811, 691. Mp: 153-155 °C.

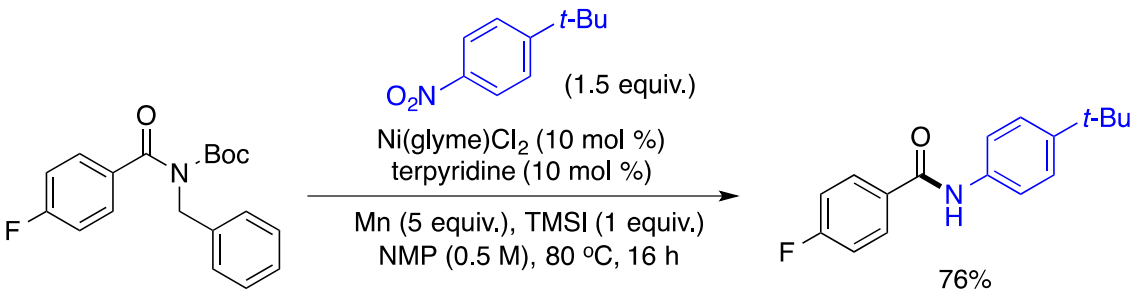


***N*-(3-Bromo-4-methylphenyl)benzamide (4c).** Following the general procedure C, the title compound was prepared using *tert*-butyl benzoyl(benzyl)carbamate (0.30 mmol, 93 mg), 2-bromo-4-

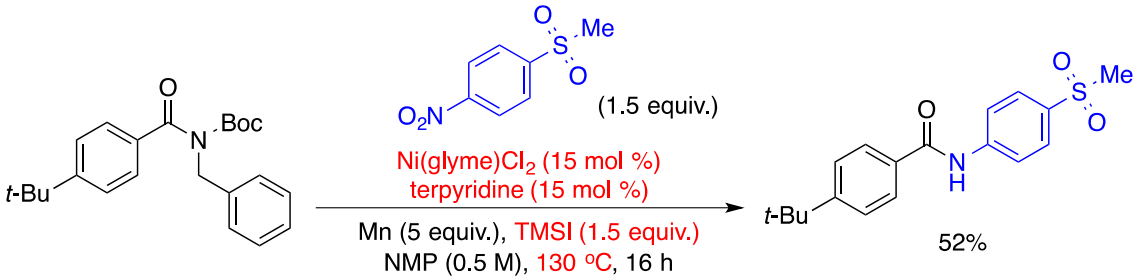
nitrotoluene (0.45 mmol, 97 mg), Ni(glyme)Cl_2 (7.5 mol %, 5.0 mg), terpyridine (7.5 mol %, 5.3 mg), Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 80 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (61 mg, 69%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.15 (s, 1 H), 7.93 (d, *J* = 1.5 Hz, 1 H), 7.84 (d, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 1.8 Hz, 1 H), 7.47-7.44 (ovrlp, 3 H), 7.20 (d, *J* = 8.2 Hz, 1 H), 2.37 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 166.1, 137.4, 135.1, 134.3, 132.3, 131.1, 129.1, 127.4, 125.0, 124.4, 119.8, 22.4. **HRMS** (ESI): Calcd for $C_{14}H_{13}BrNO$ [M+H]: 290.0189; Found: 290.0181. **IR** (neat, cm^{-1}): 3282, 1644, 1578, 1507, 1491, 1307, 1255, 1035, 858, 812, 690. 670. Mp: 135-137 °C.



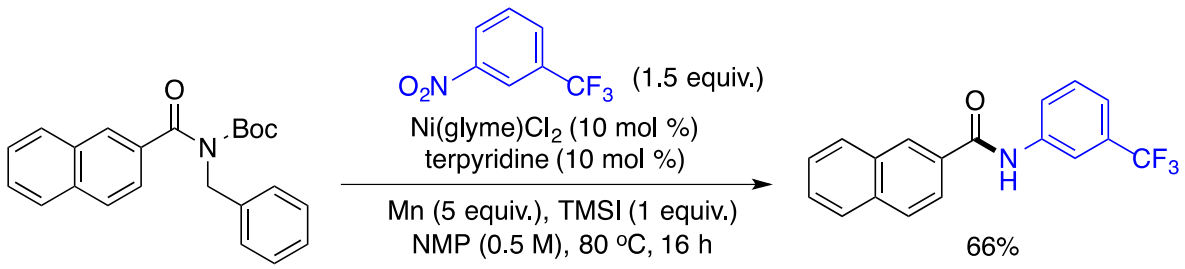
***N*-(4-(2-Fluoropyridin-3-yl)phenyl)benzamide (4d).** Following the general procedure C, the title compound was prepared using *tert*-butyl benzoyl(benzyl)carbamate (0.30 mmol, 93 mg), 2-fluoro-3-(4-nitrophenyl)pyridine (0.45 mmol, 98 mg), Ni(glyme)Cl_2 (15 mol %, 9.9 mg), terpyridine (15 mol %, 10.5 mg), Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 120 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (3:1) as an eluent to afford the title compound as an off-white amorphous solid (70 mg, 80%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.17 (s, 1 H), 8.01 (s, 1 H), 7.94-7.87 (ovrlp, 3 H), 7.79 (d, *J* = 7.6 Hz, 2 H), 7.62-7.58 (ovrlp, 3 H), 7.53 (t, *J* = 6.4 Hz, 2 H), 7.31 (t, *J* = 6.5 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.9, 159.7 (d, J_{CF} = 235.6 Hz), 146.1 (d, J_{CF} = 14.8 Hz), 141.1 (d, J_{CF} = 4.2 Hz), 139.5, 134.8, 131.8, 129.2 (d, J_{CF} = 3.0 Hz), 128.5, 127.8, 122.8 (d, J_{CF} = 4.0 Hz), 122.7 (d, J_{CF} = 27.7 Hz), 120.5, 118.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -74.1. **HRMS** (ESI): Calcd for $C_{18}H_{14}FN_2O$ [M+H]: 293.1090; Found: 293.1104. **IR** (neat, cm^{-1}): 3368, 1660, 1591, 1518, 1429, 1395, 1317, 1238, 832, 792, 713. Mp: 193-195 °C.



***N*-(4-(*tert*-Butyl)phenyl)-4-fluorobenzamide (4e).**[8] Following the general procedure C, the title compound was prepared using *tert*-butyl benzyl(4-fluorobenzoyl)carbamate (0.30 mmol, 99 mg), 1-(*tert*-butyl)-4-nitrobenzene (0.45 mmol, 81 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), terpyridine (10 mol %, 7.0 mg), Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 80 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (62 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (s, 1 H), 7.85 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{CF}$ = 5.6 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.10 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{CF}$ = 8.1 Hz, 2 H), 1.32 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.93 (d, $^1J_{CF}$ = 250.9 Hz), 164.91, 147.9, 135.3, 131.3 (d, $^4J_{CF}$ = 3.1 Hz), 129.6 (d, $^3J_{CF}$ = 8.9 Hz), 126.0, 120.4, 115.9 (d, $^2J_{CF}$ = 21.8 Hz), 34.6, 31.5. **IR** (neat, cm^{-1}): 3312, 1644, 1601, 1503, 1330, 1226, 1160, 840, 758, 665.

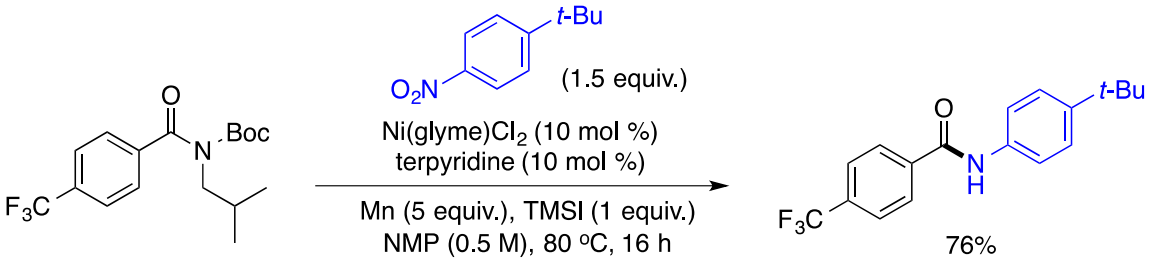


4-(*tert*-Butyl)-*N*-(4-(methylsulfonyl)phenyl)benzamide (4f).[8] Following the general procedure C, the title compound was prepared using *tert*-butyl benzyl(4-(*tert*-butyl)benzoyl)carbamate (1 equiv, 0.35 mmol, 129 mg), 1-(methylsulfonyl)-4-nitrobenzene (1.5 equiv, 0.525 mmol, 106 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), terpyridine (15 mol %, 12.2 mg), Mn (5 equiv, 1.75 mmol, 96 mg), TMSI (1.5 equiv, 0.525 mmol, 75 μL), and NMP (0.7 mL) at the reaction temperature of 130 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (4:1) as an eluent to afford the title compound as a pale brown amorphous solid (57 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.60 (s, 1 H), 7.88-7.80 (ovrlp, 6 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 3.02 (s, 3 H), 1.33 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 156.2, 143.4, 135.1, 131.2, 128.6, 127.3, 125.9, 120.3, 44.8, 35.1, 31.2. **IR** (neat, cm^{-1}): 3360, 1675, 1590, 1505, 1298, 1141, 964, 831, 768.



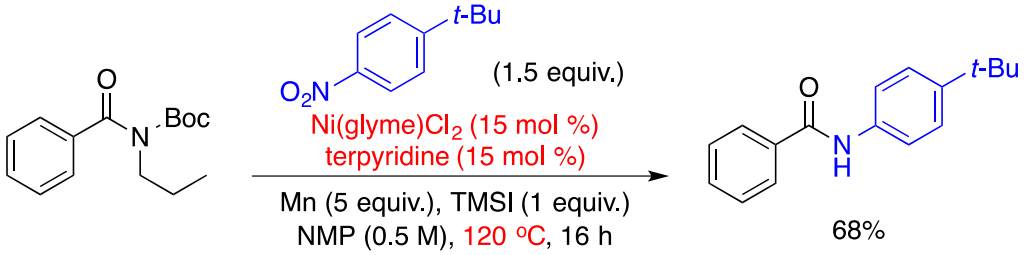
***N*-(3-(Trifluoromethyl)phenyl)-2-naphthamide (4g).**[8] Following the general procedure C, the title compound was prepared using *tert*-butyl (2-naphthoyl)(benzyl)carbamate (0.30 mmol, 108 mg), 3-nitrobenzotrlfluoride (0.45 mmol, 86 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), terpyridine (10 mol %,

7.0 mg), Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 80 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as an off-white amorphous solid (62 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (s, 1 H), 8.27 (s, 1 H), 7.98 (s, 1 H), 7.93-7.85 (ovrlp, 5 H), 7.60-7.52 (ovrlp, 2 H), 7.47 (t, J = 8.0 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.7, 135.1, 132.7, 131.7, 131.6 (q, $^2J_{CF}$ = 32.3 Hz), 129.8, 129.1, 129.0, 128.3, 128.1, 128.0, 127.8, 127.2 (q, $^1J_{CF}$ = 270.6 Hz), 123.52, 123.46 (q, $^4J_{CF}$ = 0.8 Hz), 121.2 (q, $^3J_{CF}$ = 3.8 Hz), 117.1 (q, $^3J_{CF}$ = 4.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -65.9. **IR** (neat, cm^{-1}): 3261, 1649, 1552, 1446, 1325, 1165, 1108, 1068, 800, 778.



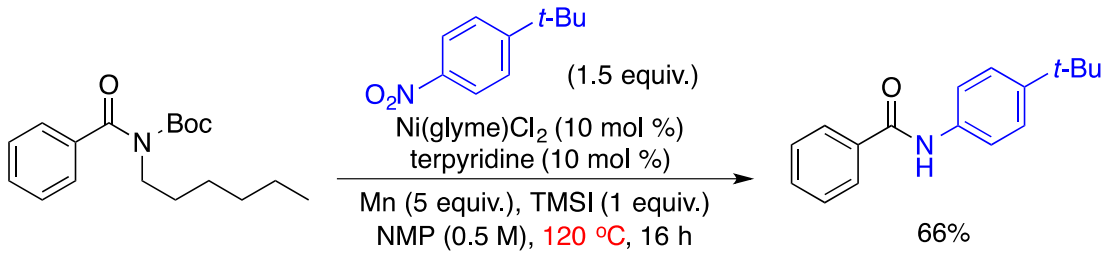
***N*-(4-(*tert*-Butyl)phenyl)-4-(trifluoromethyl)benzamide (4h).**[21] Following the general procedure C, the title compound was prepared using *tert*-butyl isobutyl(4-(trifluoromethyl)benzoyl)carbamate (0.30 mmol, 104 mg), 1-(*tert*-butyl)-4-nitrobenzene (0.45 mmol, 81 mg), Ni(glyme)Cl_2 (10 mol %, 6.6 mg), terpyridine (10 mol %, 7.0 mg), Mn (5 equiv, 1.5 mmol, 83 mg), TMSI (1 equiv, 0.30 mmol, 43 μL), and NMP (0.6 mL) at the reaction temperature of 80 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale brown amorphous solid (73 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.69 (s, 1 H), 7.85 (d, J = 7.9 Hz, 2 H), 7.55-7.52 (ovrlp, 4 H), 7.31 (d, J = 8.4 Hz, 2 H), 1.30 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.2, 148.2, 138.3, 135.1, 133.3 (q, $^2J_{CF}$ = 32.5 Hz), 127.8, 125.9, 125.6 (q, $^3J_{CF}$ = 3.7 Hz), 123.7 (q, $^1J_{CF}$ = 270.9 Hz), 120.8, 34.5, 31.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -66.1. **IR** (neat, cm^{-1}): 3313, 1655, 1529, 1324, 1164, 1119, 1065, 1016, 831.

***N*-(4-(*tert*-Butyl)phenyl)benzamide (4i).**[9]

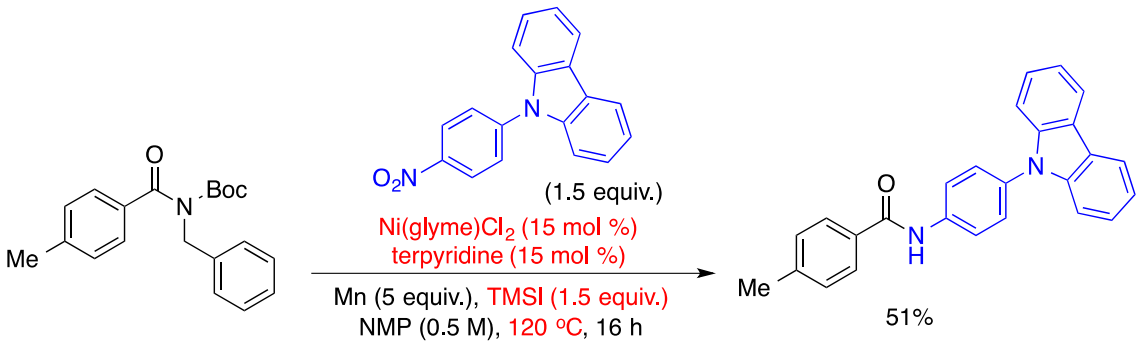


(i) From *tert*-butyl benzoyl(propyl)carbamate (P-9 of Figure 4 in maintext). Following the general procedure C, the title compound was prepared using *tert*-butyl benzoyl(propyl)carbamate (1

equiv, 0.35 mmol, 92 mg), 1-(*tert*-butyl)-4-nitrobenzene (1.5 equiv, 0.525 mmol, 94 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), terpyridine (15 mol %, 12.2 mg), Mn (5 equiv, 1.75 mmol, 96 mg), TMSI (1 equiv, 0.70 mmol, 50 μL), and NMP (0.7 mL) at the reaction temperature of 120 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale brown amorphous solid (60 mg, 68%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.96 (s, 1 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 7.58-7.53 (ovrlp, 3 H), 7.49 (t, *J* = 7.1 Hz, 2 H), 7.40 (d, *J* = 8.6 Hz, 2 H), 1.33 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.9, 147.9, 135.9, 135.6, 132.1, 129.1, 127.3, 126.2, 120.4, 34.7, 31.5. **IR** (neat, cm^{-1}): 3310, 1649, 1521, 1488, 1287, 820, 709.

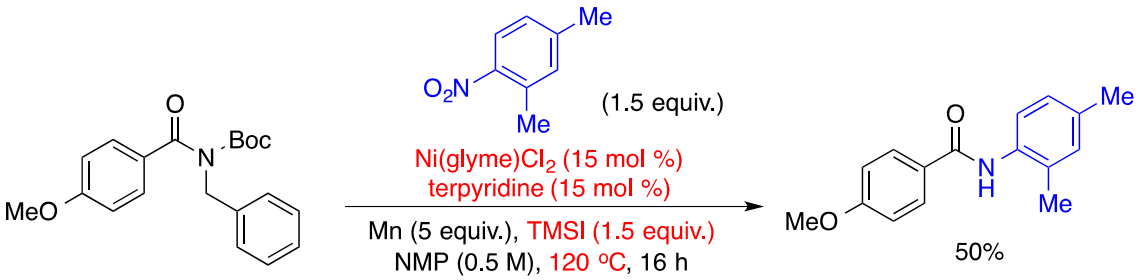


(ii) From *tert*-butyl benzoyl(hexyl)carbamate (P-10 of Figure 4 in maintext). Following the general procedure C, the title compound was prepared using *tert*-butyl benzoyl(hexyl)carbamate (1 equiv, 0.35 mmol, 107 mg), 1-(*tert*-butyl)-4-nitrobenzene (1.5 equiv, 0.525 mmol, 94 mg), Ni(glyme)Cl_2 (10 mol %, 7.7 mg), terpyridine (10 mol %, 8.1 mg), Mn (5 equiv, 1.75 mmol, 96 mg), TMSI (1 equiv, 0.70 mmol, 50 μL), and NMP (0.7 mL) at the reaction temperature of 120 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a pale brown amorphous solid (58 mg, 66%). Spectral and analytical data were identical to those reported for the same compound above.

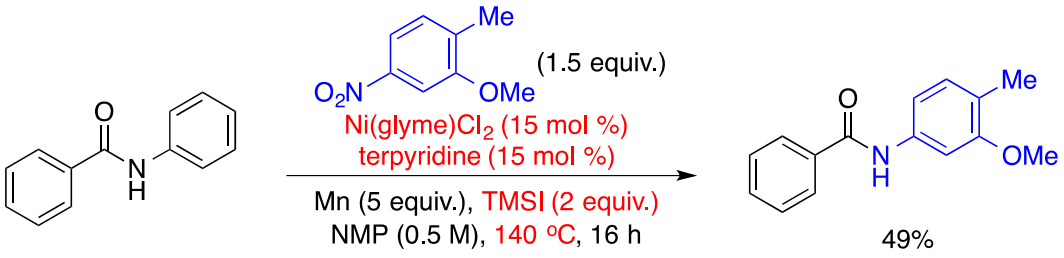


***N*-(4-(9*H*-carbazol-9-yl)phenyl)-4-methylbenzamide (4j).**[8] Following the general procedure C, the title compound was prepared using *tert*-butyl benzyl(4-methylbenzoyl)carbamate (1 equiv, 0.35 mmol, 114 mg), 9-(4-nitrophenyl)-9*H*-carbazole (1.5 equiv, 0.525 mmol, 151 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), terpyridine (15 mol %, 12.2 mg), Mn (5 equiv, 1.75 mmol, 96 mg), TMSI (1.5 equiv, 0.525 mmol, 75 μL), and NMP (0.7 mL) at the reaction temperature of 120 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (8:1) as an eluent to afford the title compound as a pale brown amorphous solid (67 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 2 H),

7.98 (s, 1 H), 7.88 (d, *J* = 8.8 Hz, 2 H), 7.83 (d, *J* = 8.2 Hz, 2 H), 7.55 (d, *J* = 8.7 Hz, 2 H), 7.43-7.38 (ovrlp, 4 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.30-7.26 (m, 2 H), 2.45 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 142.8, 141.1, 137.4, 133.8, 131.9, 129.6, 127.9, 127.3, 126.1, 123.4, 121.7, 120.4, 120.0, 109.8, 21.6. **IR** (neat, cm^{-1}): 3258, 1647, 1517, 1449, 1314, 1225, 740, 717.



***N*-(2,4-dimethylphenyl)-4-methoxybenzamide (4k).** Following the general procedure C, the title compound was prepared using *tert*-butyl benzyl(4-methoxybenzoyl)carbamate (1 equiv, 0.35 mmol, 119 mg), 2,4-dimethylnitrobenzene (1.5 equiv, 0.525 mmol, 82 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), terpyridine (15 mol %, 12.2 mg), Mn (5 equiv, 1.75 mmol, 96 mg), TMSI (1.5 equiv, 0.525 mmol, 75 μL), and NMP (0.7 mL) at the reaction temperature of 120 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a pale brown amorphous solid (45 mg, 50%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.84 (d, *J* = 8.8 Hz, 2 H), 7.66-7.60 (ovrlp, 2 H), 7.06 (s, 1 H), 7.04 (d, *J* = 8.2 Hz, 1 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 2.32 (s, 3 H), 2.27 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.4, 162.8, 135.5, 133.9, 131.5, 130.8, 129.3, 127.6, 127.5, 124.1, 114.2, 55.9, 21.0, 18.0. **HRMS** (ESI): Calcd for $C_{16}H_{18}NO_2$ [M+H]: 256.1338; Found: 256.1353. **IR** (neat, cm^{-1}): 3270, 1638, 1606, 1509, 1301, 1253, 1176, 1025, 843, 682. Mp: 152-154 °C.



***N*-(3-methoxy-4-methylphenyl)benzamide (4l).**[8] Following the general procedure C, the title compound was prepared using *N*-phenylbenzamide (1 equiv, 0.35 mmol, 69 mg), 2-methoxy-1-methyl-4-nitrobenzene (1.5 equiv, 0.525 mmol, 88 mg), Ni(glyme)Cl_2 (15 mol %, 11.6 mg), terpyridine (15 mol %, 12.2 mg), Mn (5 equiv, 1.75 mmol, 96 mg), TMSI (2 equiv, 0.70 mmol, 100 μL), and NMP (0.7 mL) at the reaction temperature of 140 °C. The crude product was purified by preparative TLC using hexanes/EtOAc (8:1) as an inseparable mixture of title compound and starting material (*N*-phenylbenzamide). The yield of title compound was calculated by comparing the ratio of title compound and starting material by ^{1}H NMR spectroscopy of the separated product (42 mg, 49%).

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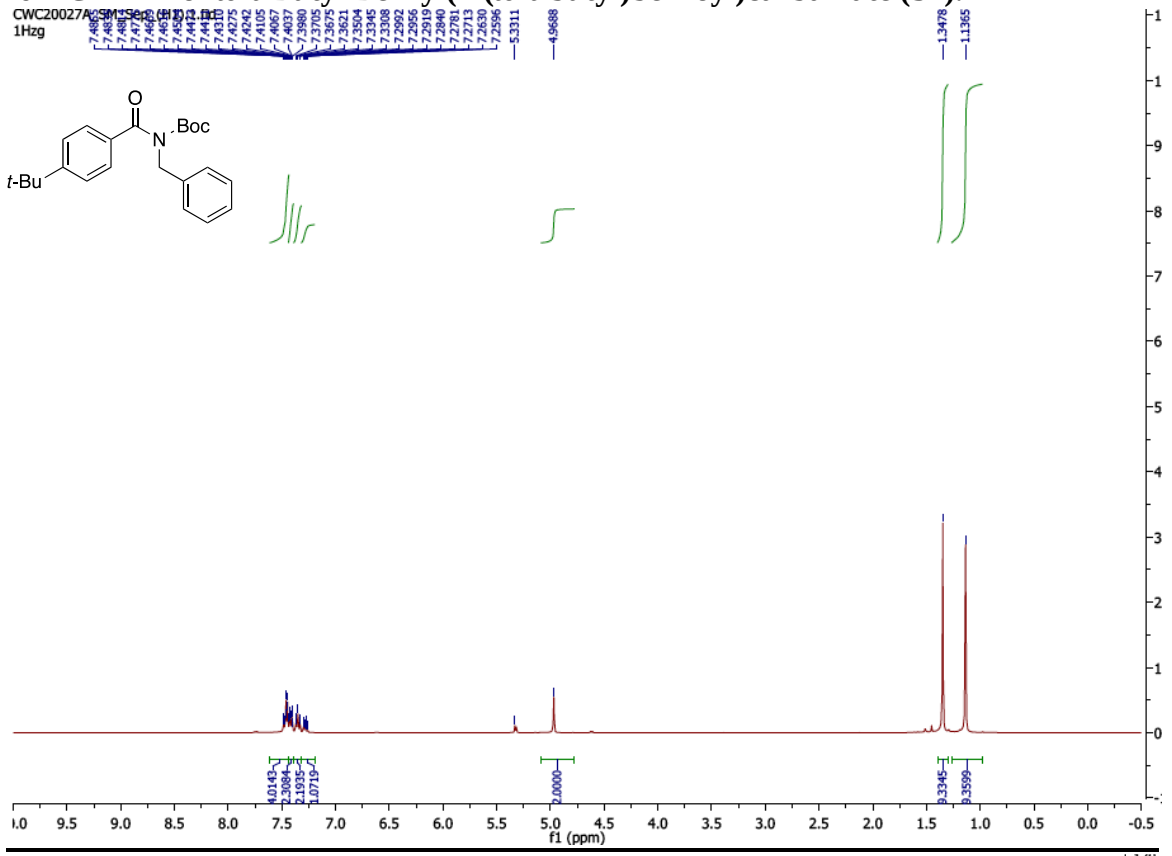
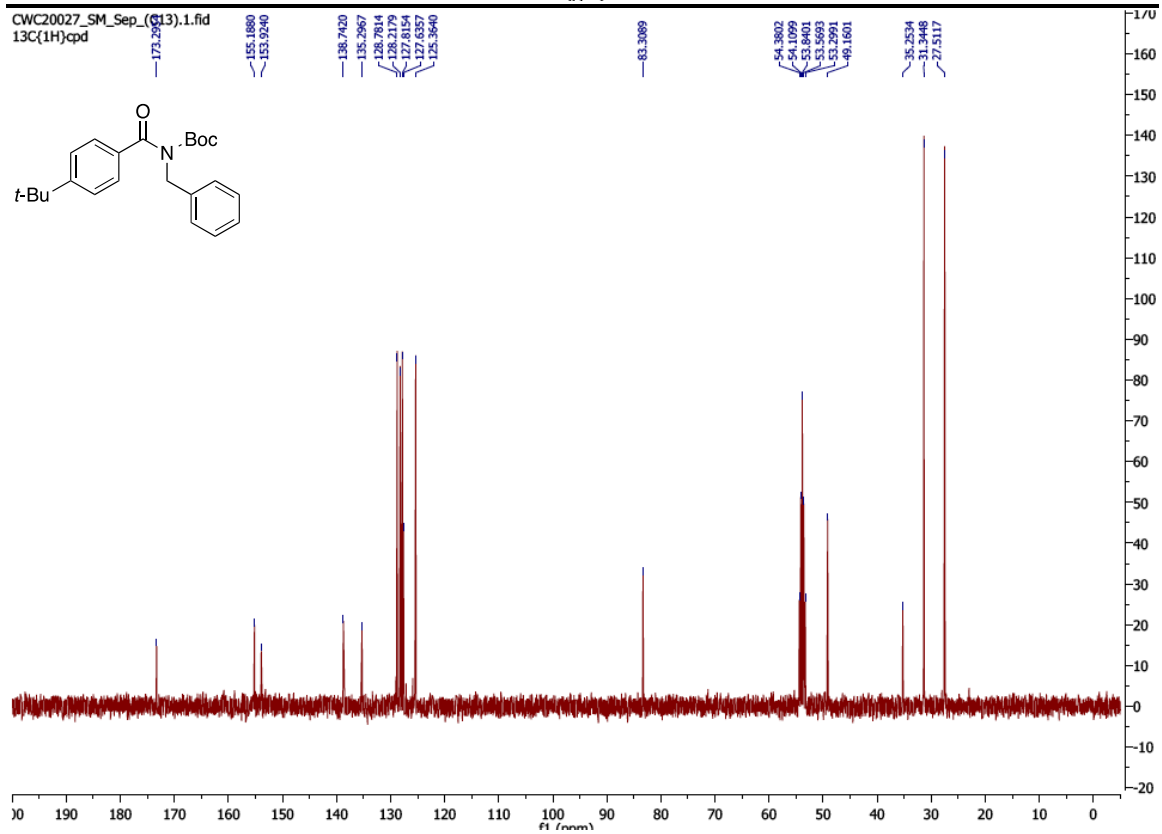
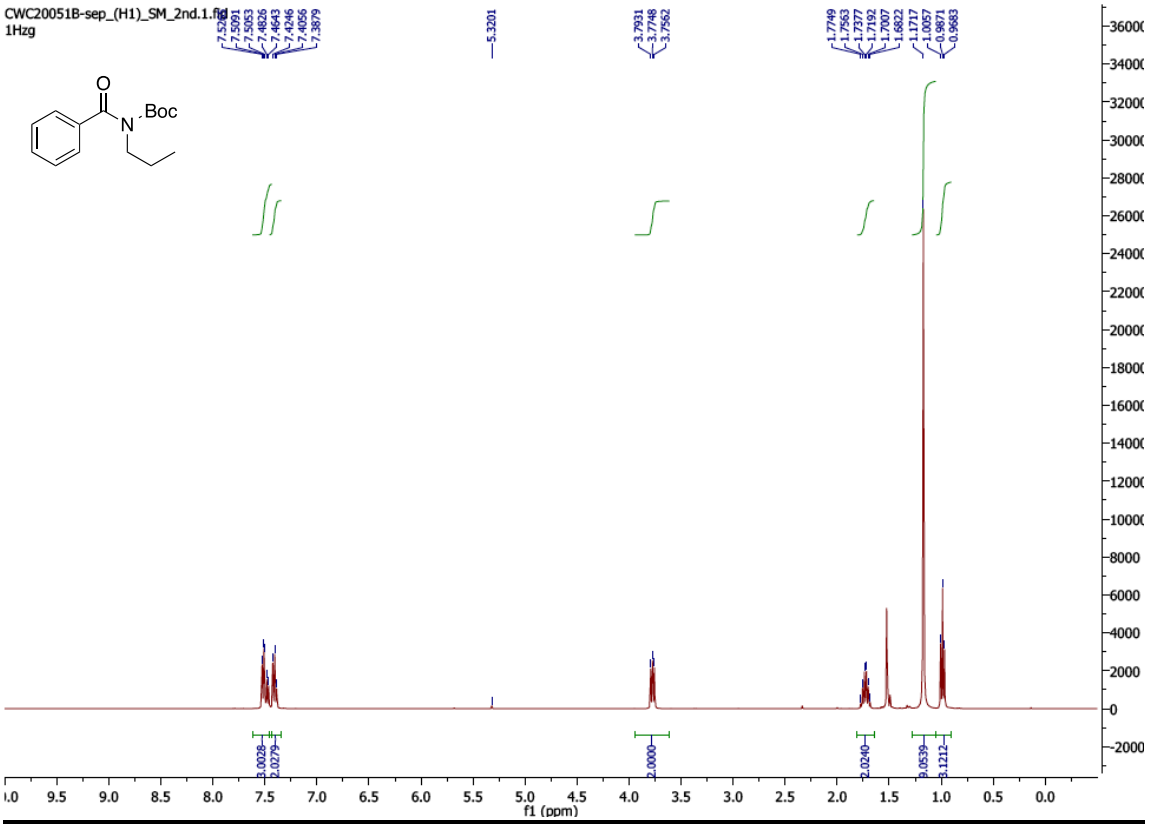
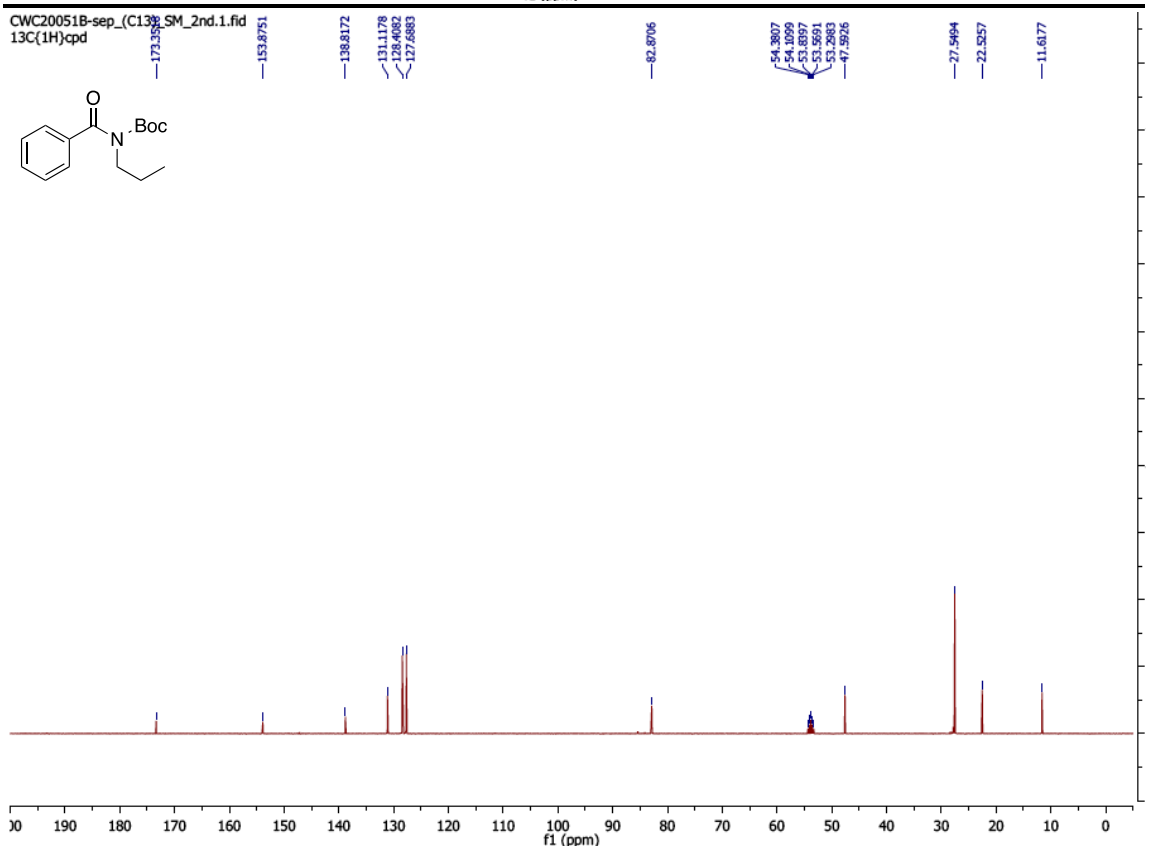
^{1}H and ^{13}C NMR of *tert*-Butyl Benzyl(4-(*tert*-butyl)benzoyl)carbamate (S1).



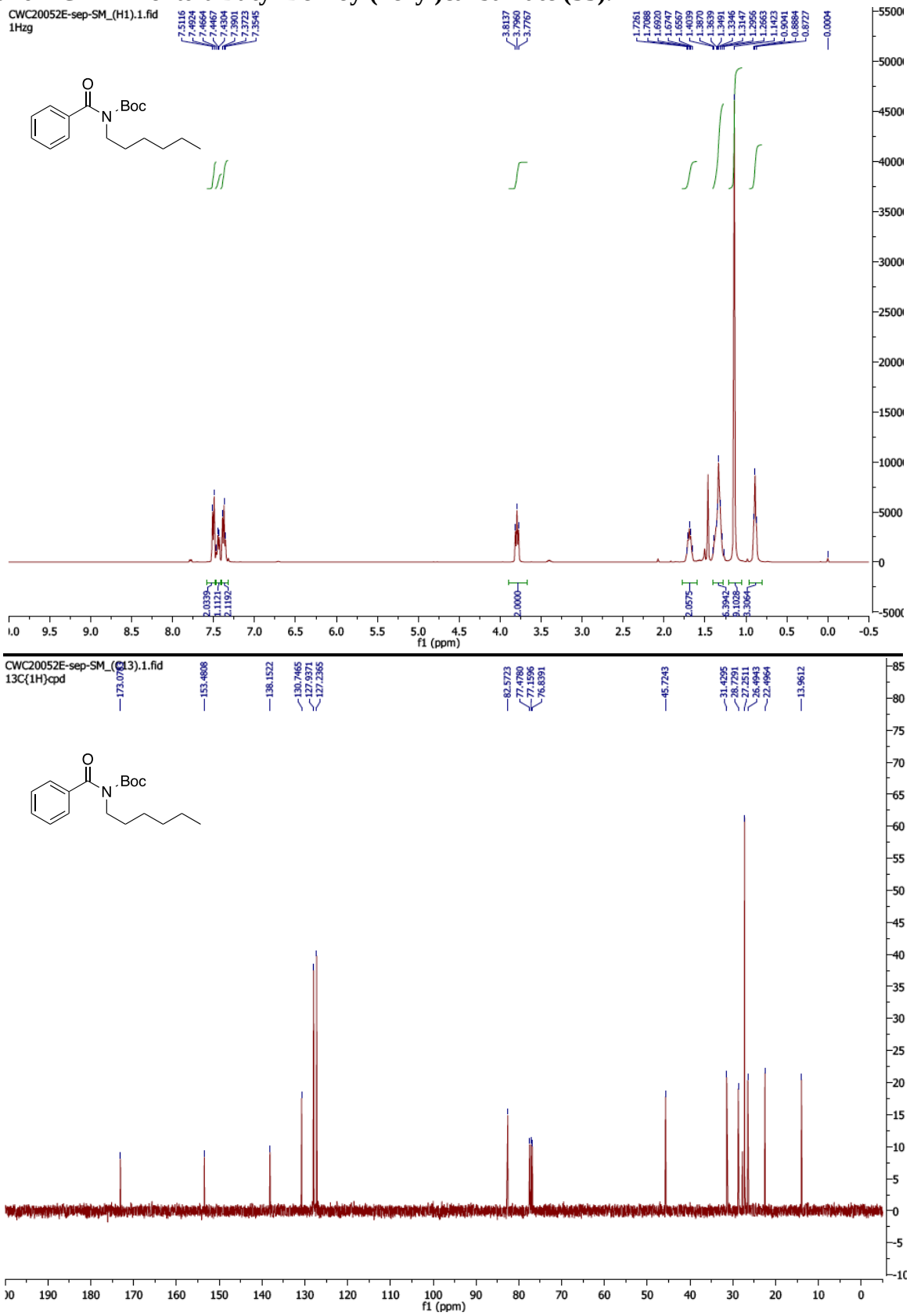


^{1}H and ^{13}C NMR of *tert*-Butyl Benzoyl(propyl)carbamate (S2).

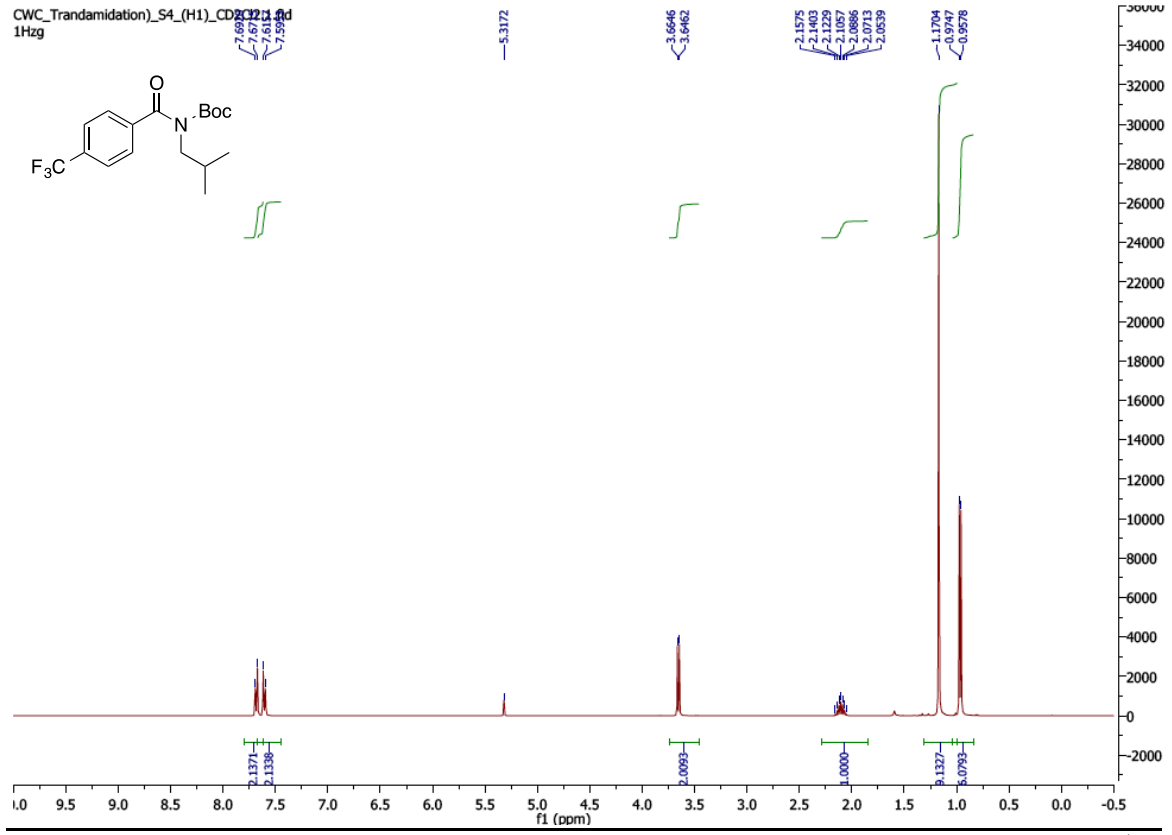


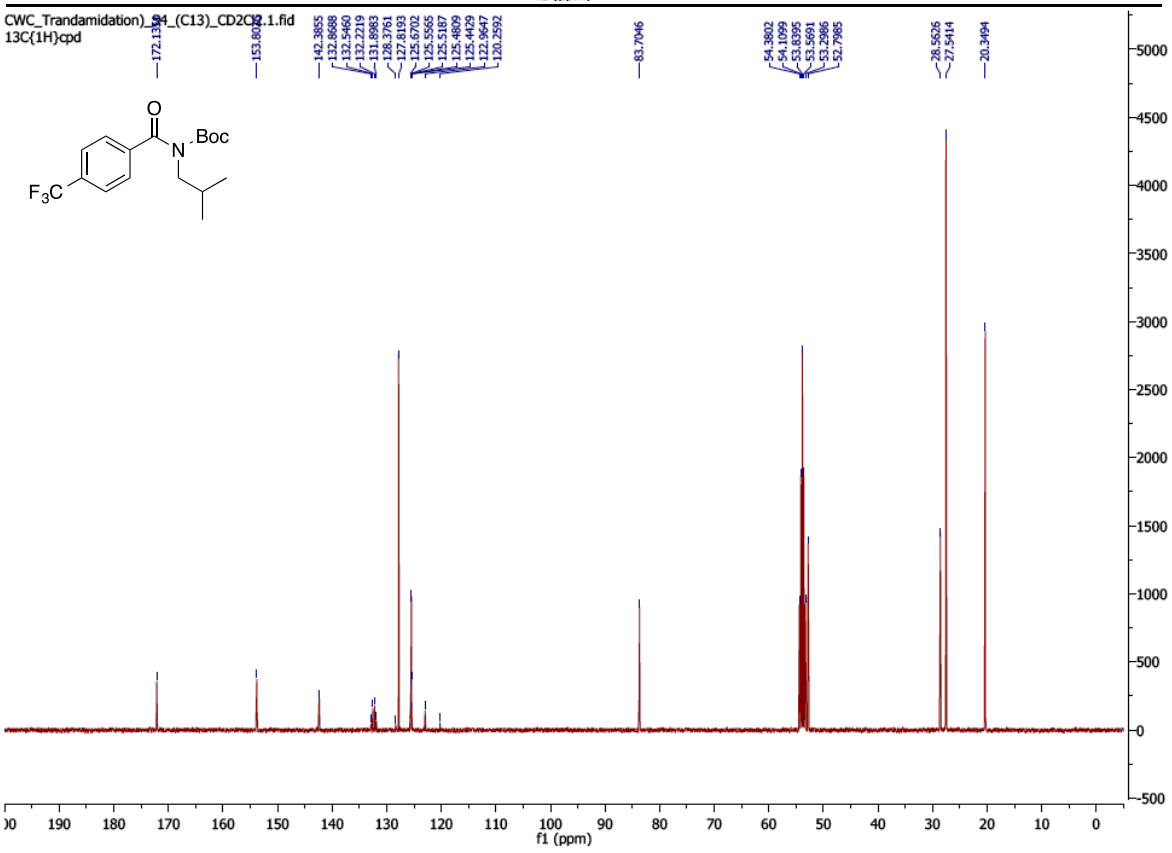


^{1}H and ^{13}C NMR of *tert*-Butyl Benzoyl(hexyl)carbamate (S3).

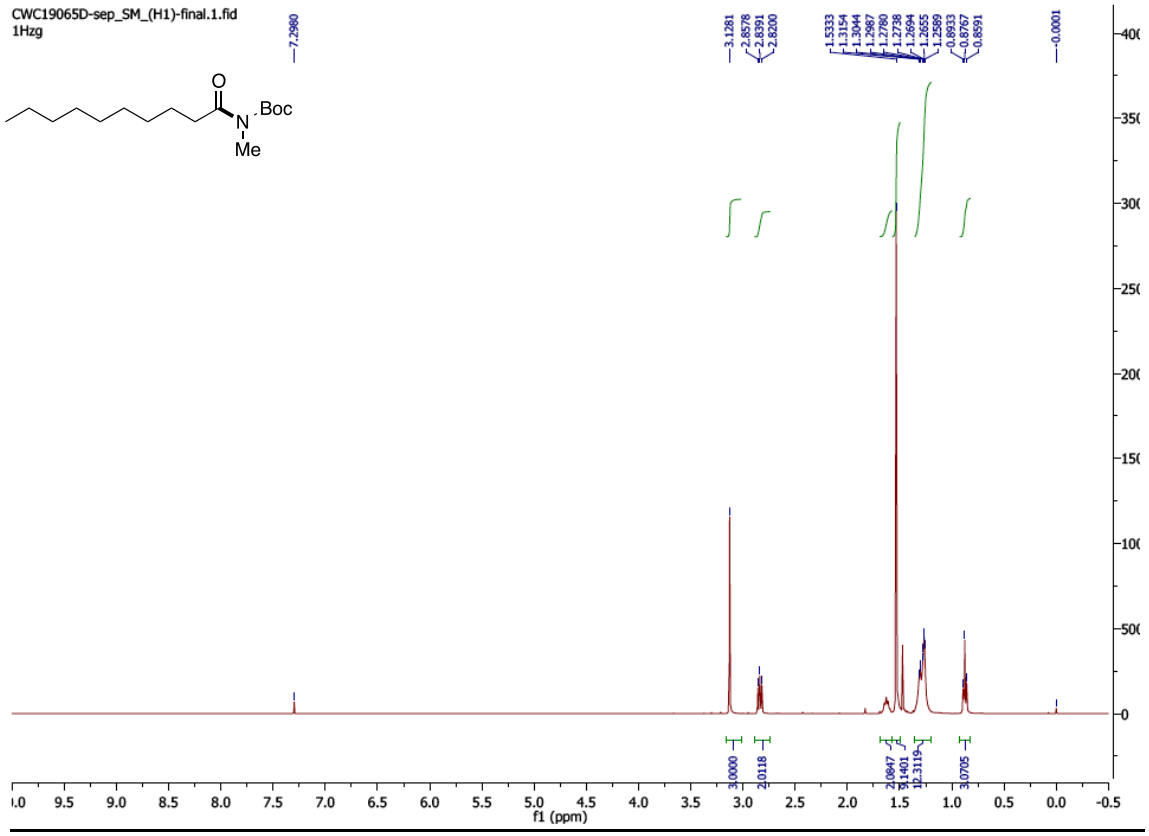


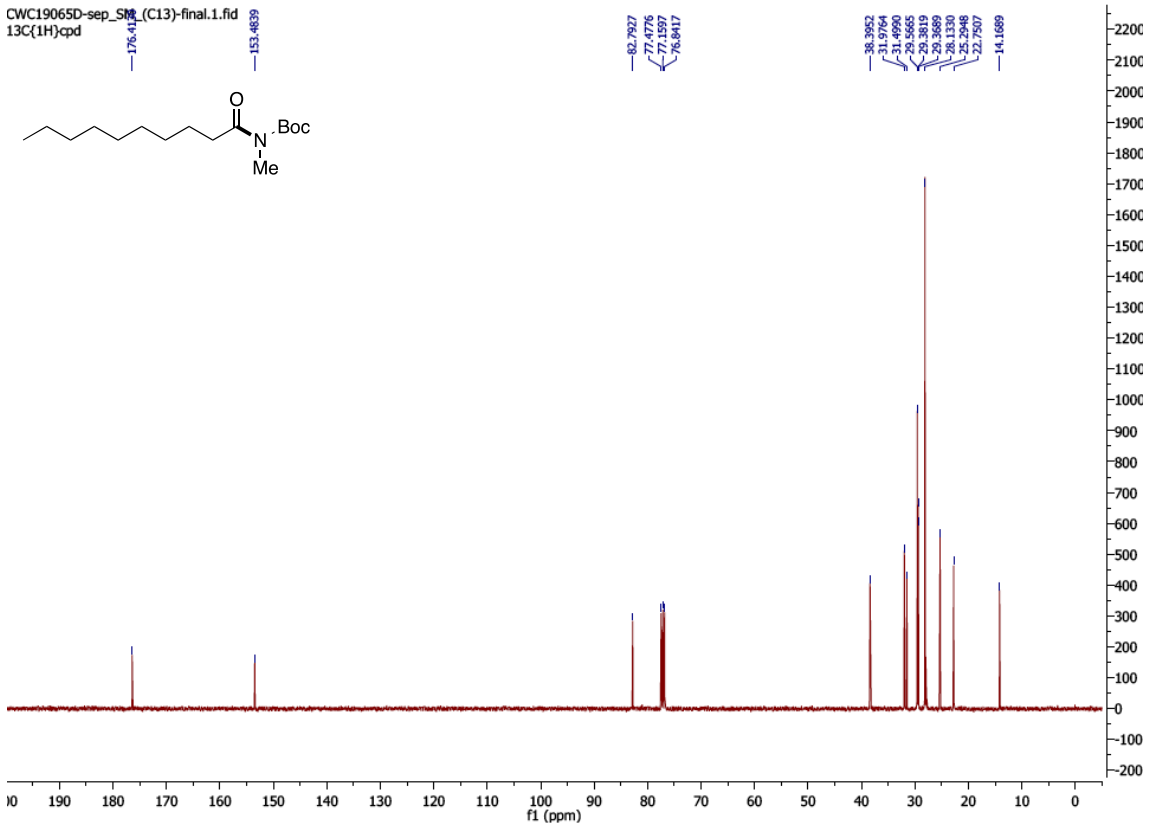
^{1}H and ^{13}C NMR of *tert*-Butyl Isobutyl(4-(trifluoromethyl)benzoyl)carbamate (S4).



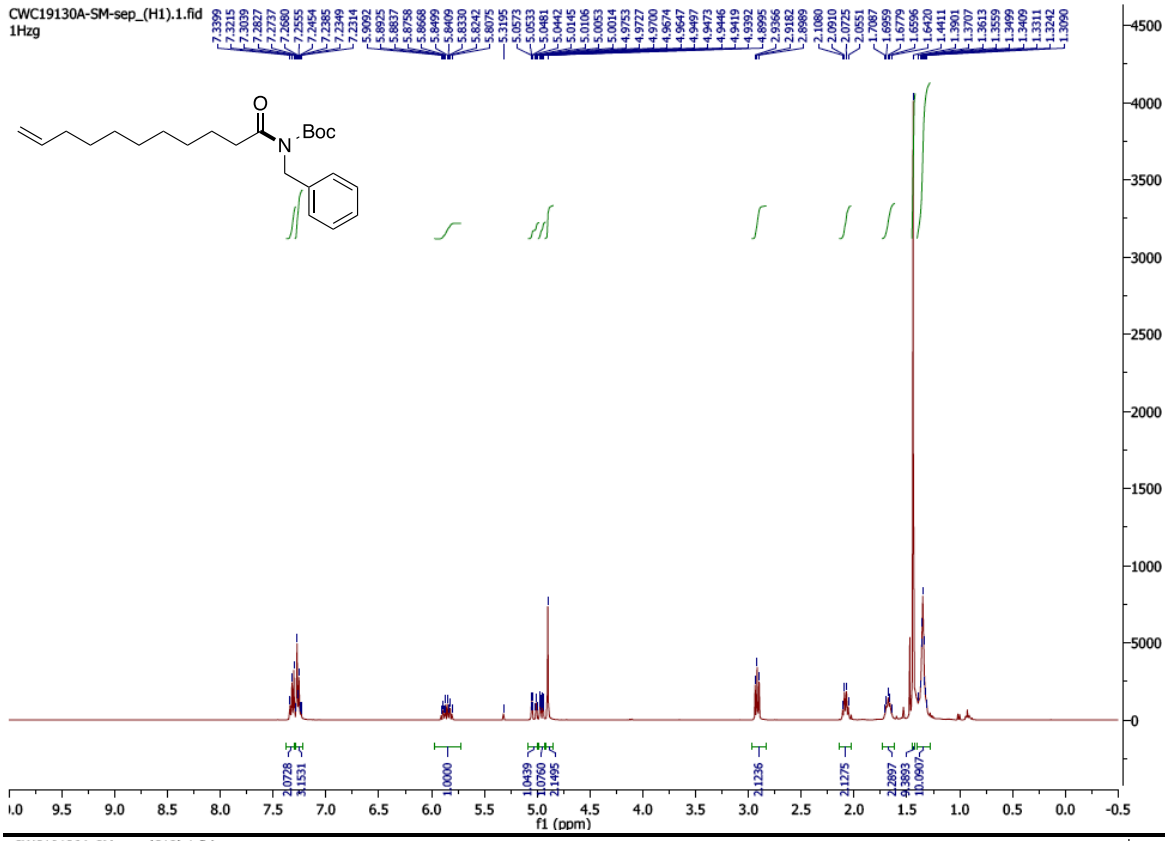


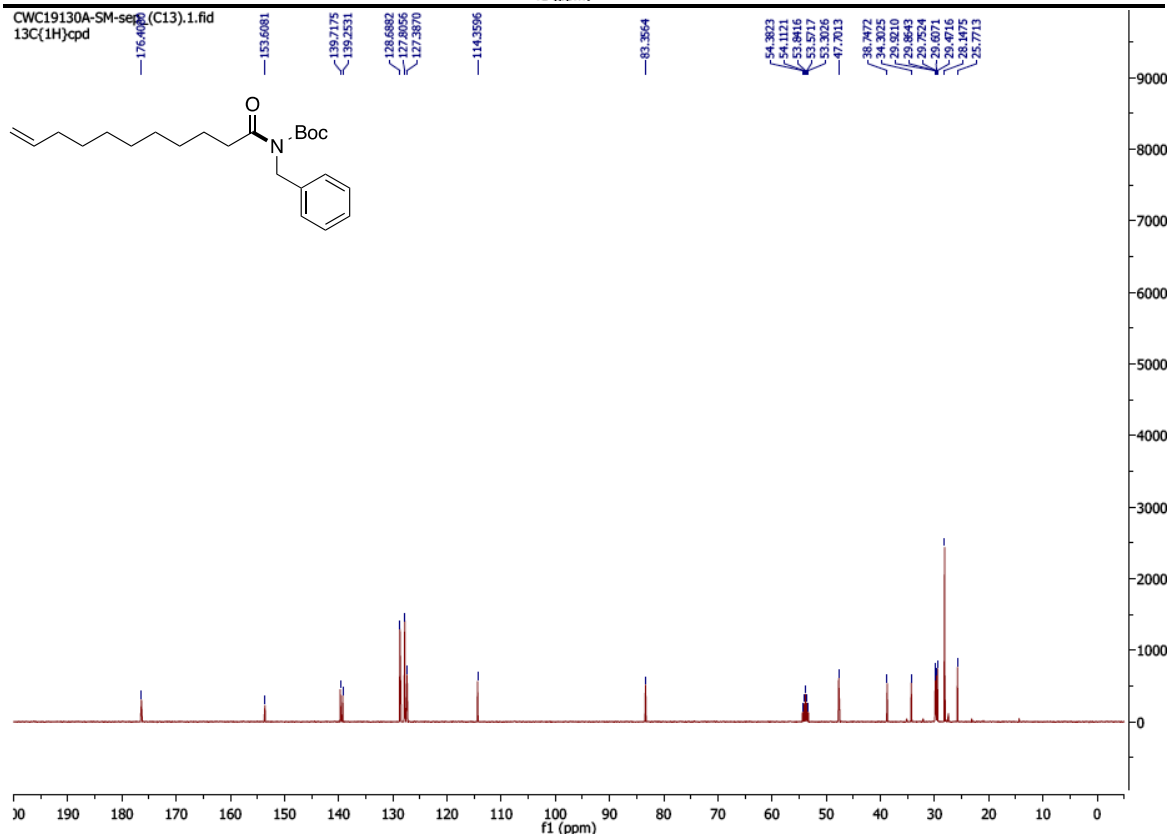
^{1}H and ^{13}C NMR of *tert*-Butyl Decanoyl(methyl)carbamate (S5).



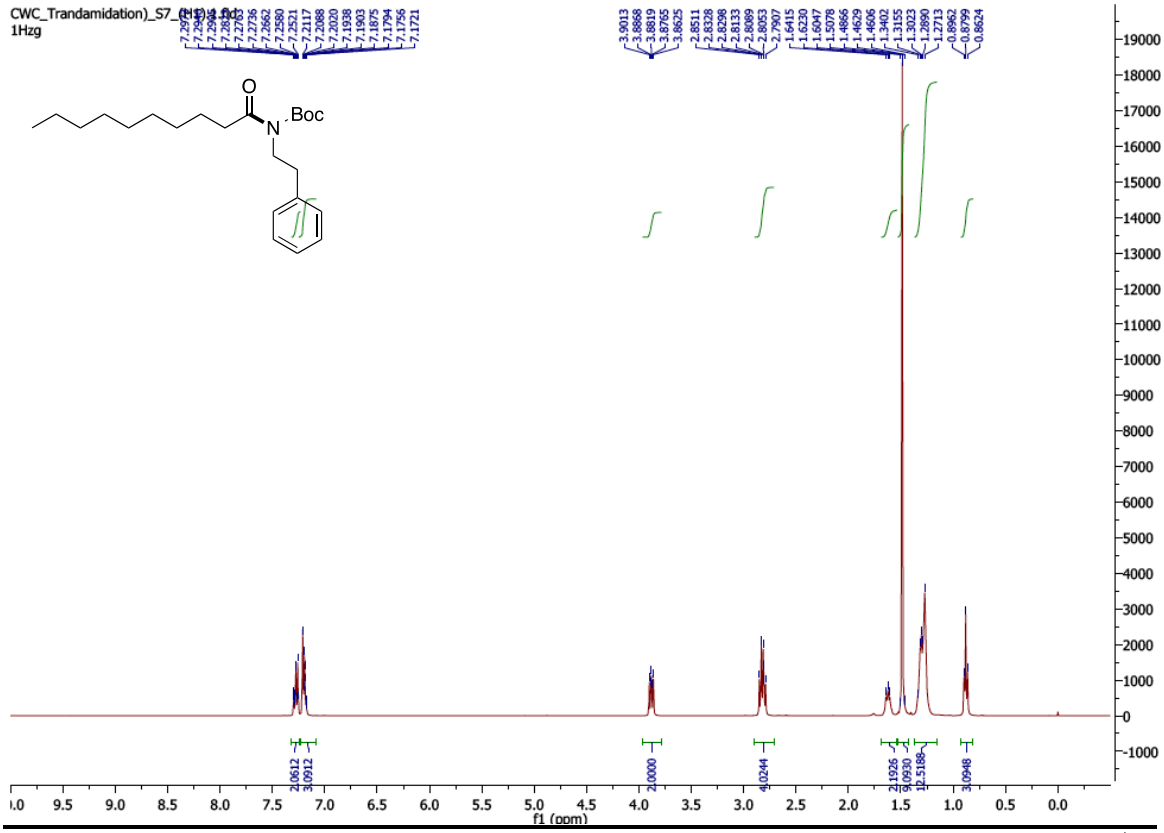


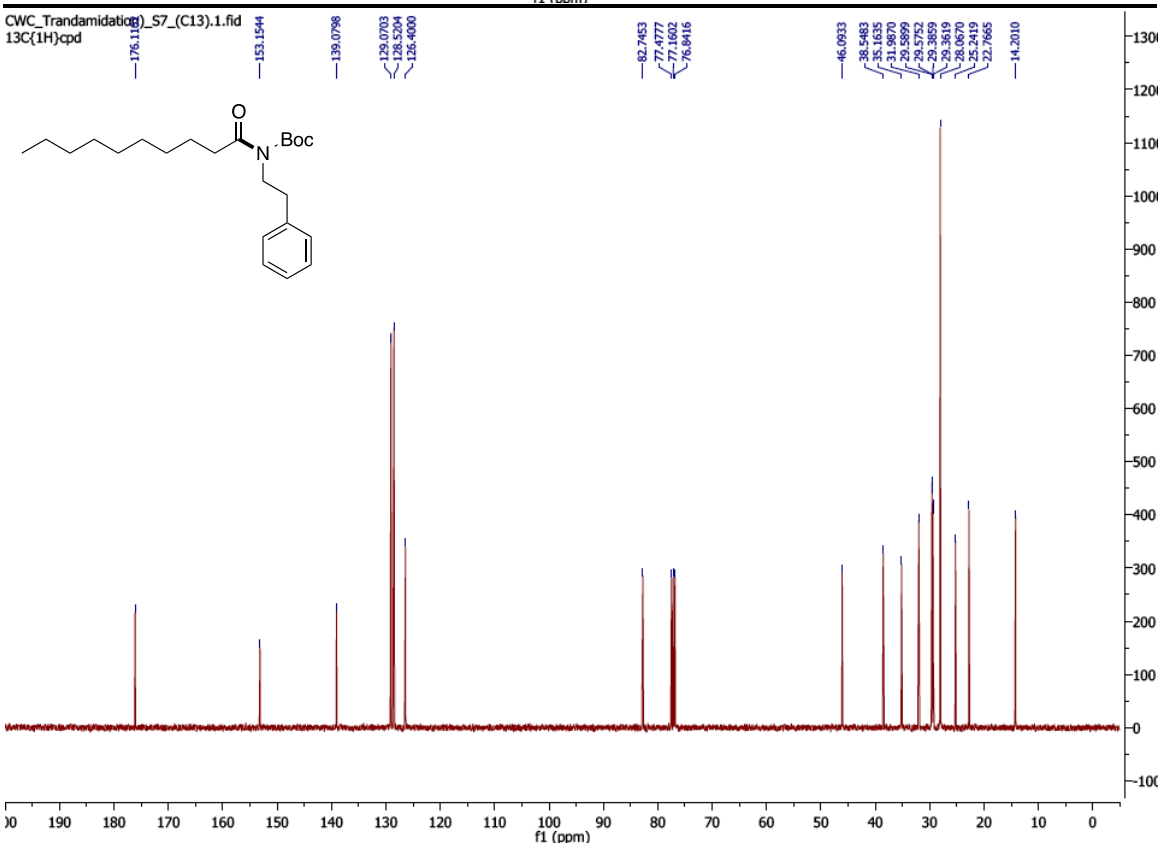
^{1}H and ^{13}C NMR of *tert*-Butyl Benzyl(undec-10-enoyl)carbamate (S6).



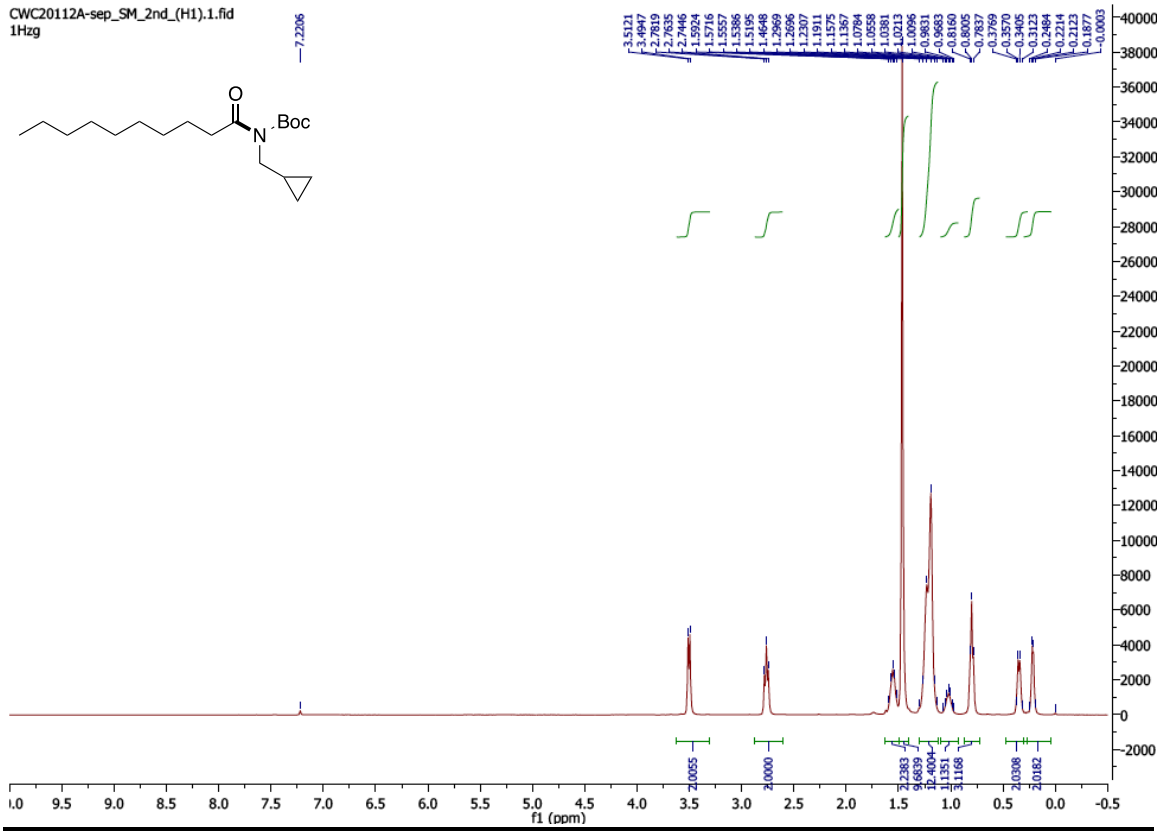


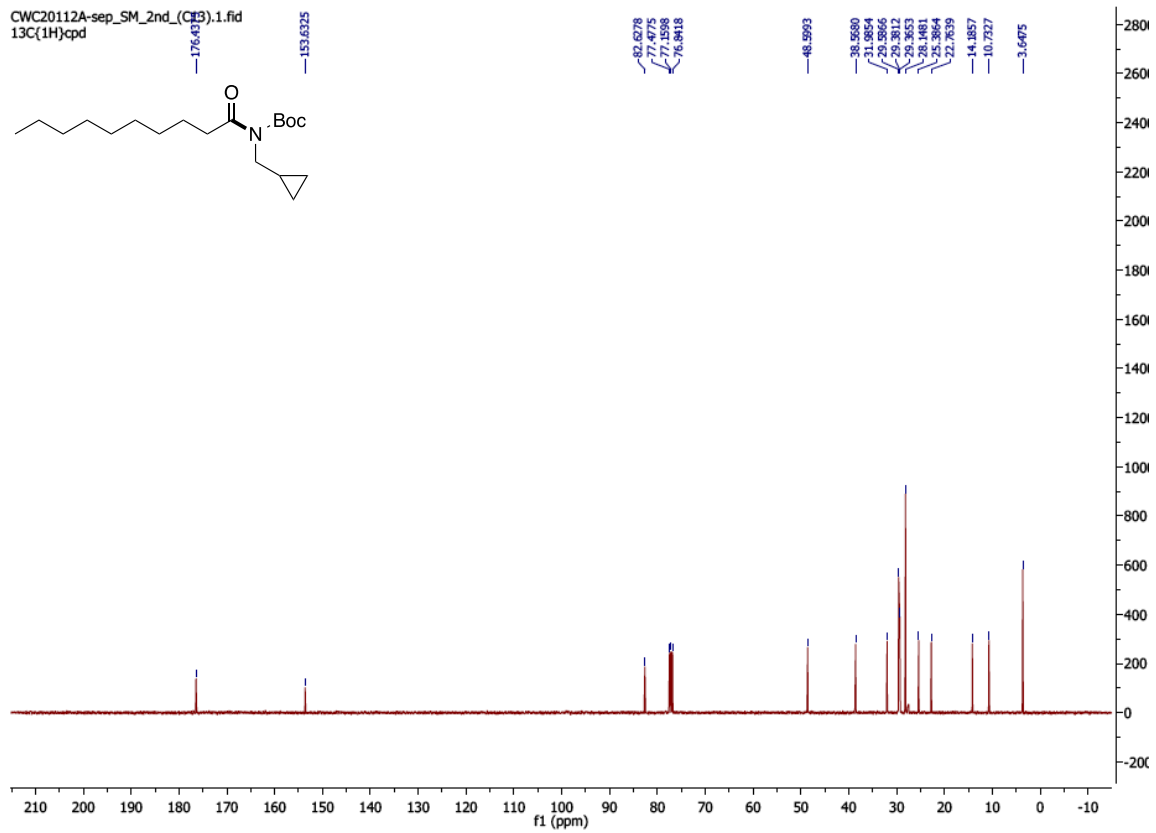
^{1}H and ^{13}C NMR of *tert*-Butyl Decanoyl(phenethyl)carbamate (S7).



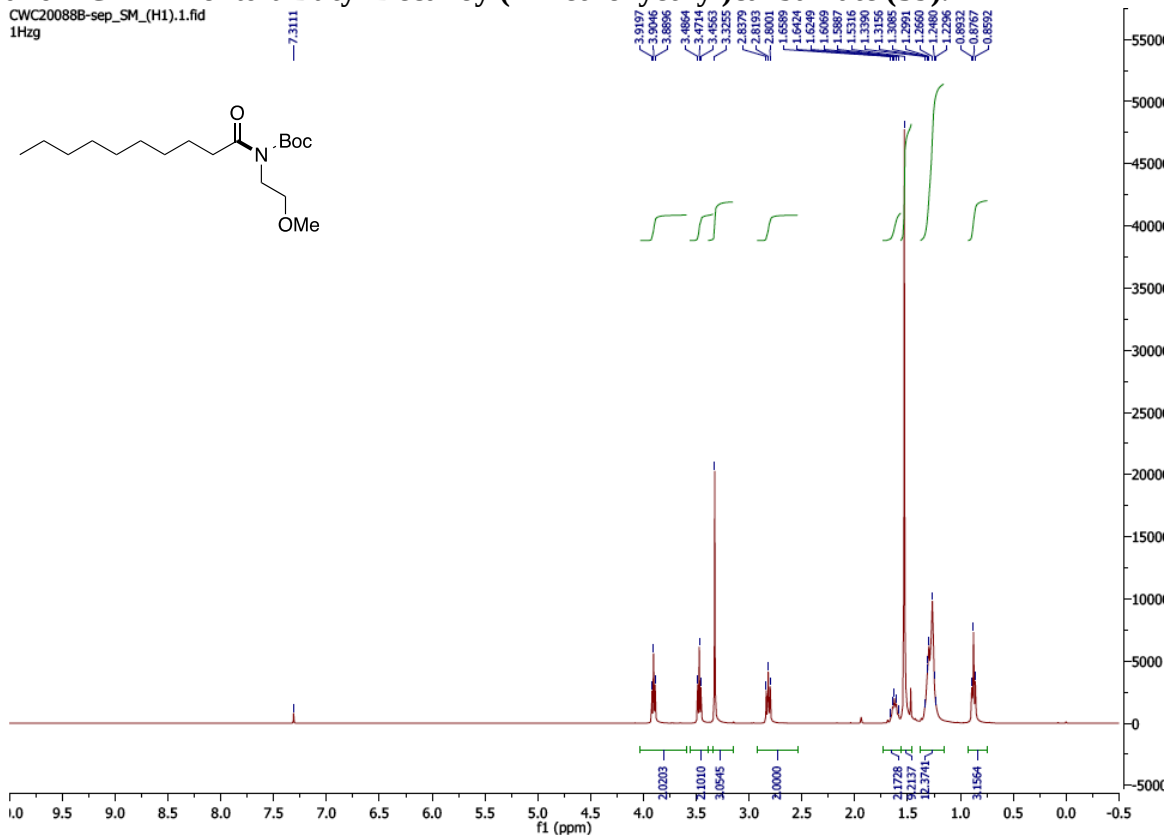


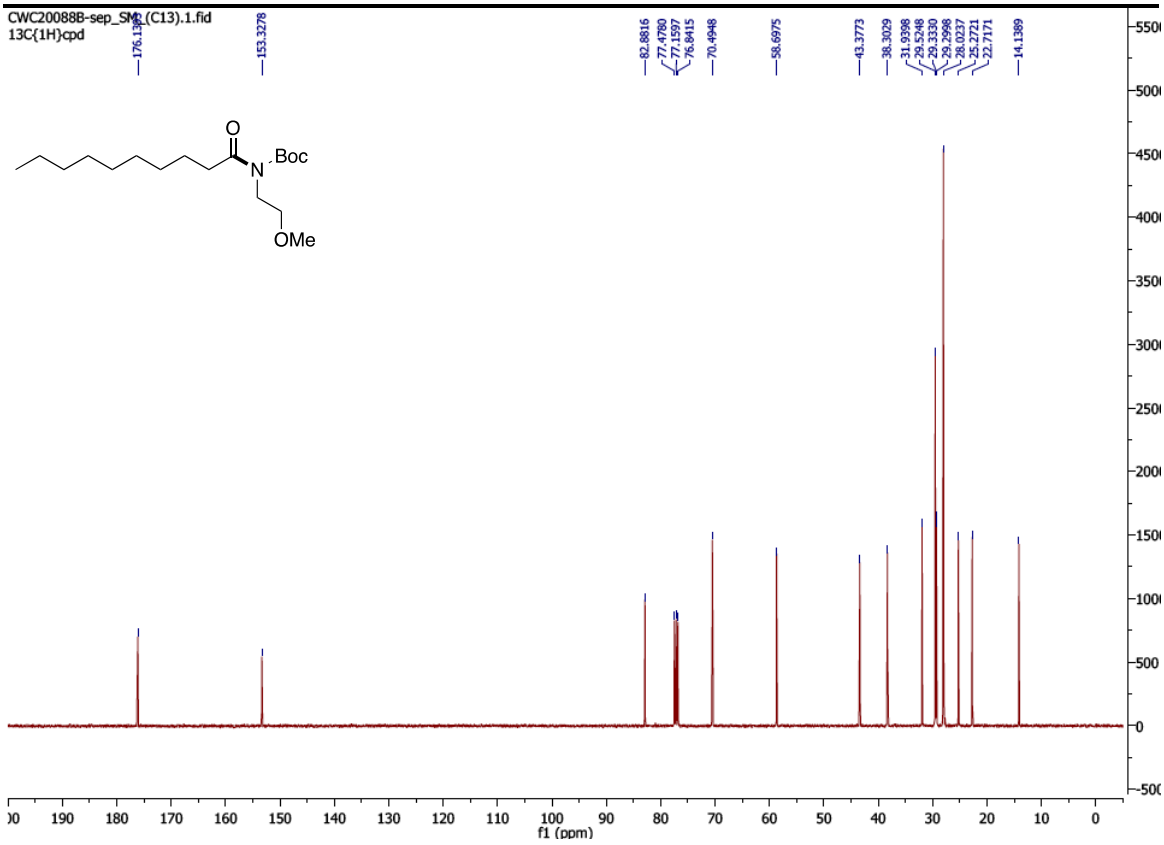
^{1}H and ^{13}C NMR of *tert*-Butyl (Cyclopropylmethyl)(decanoyl)carbamate (S8).



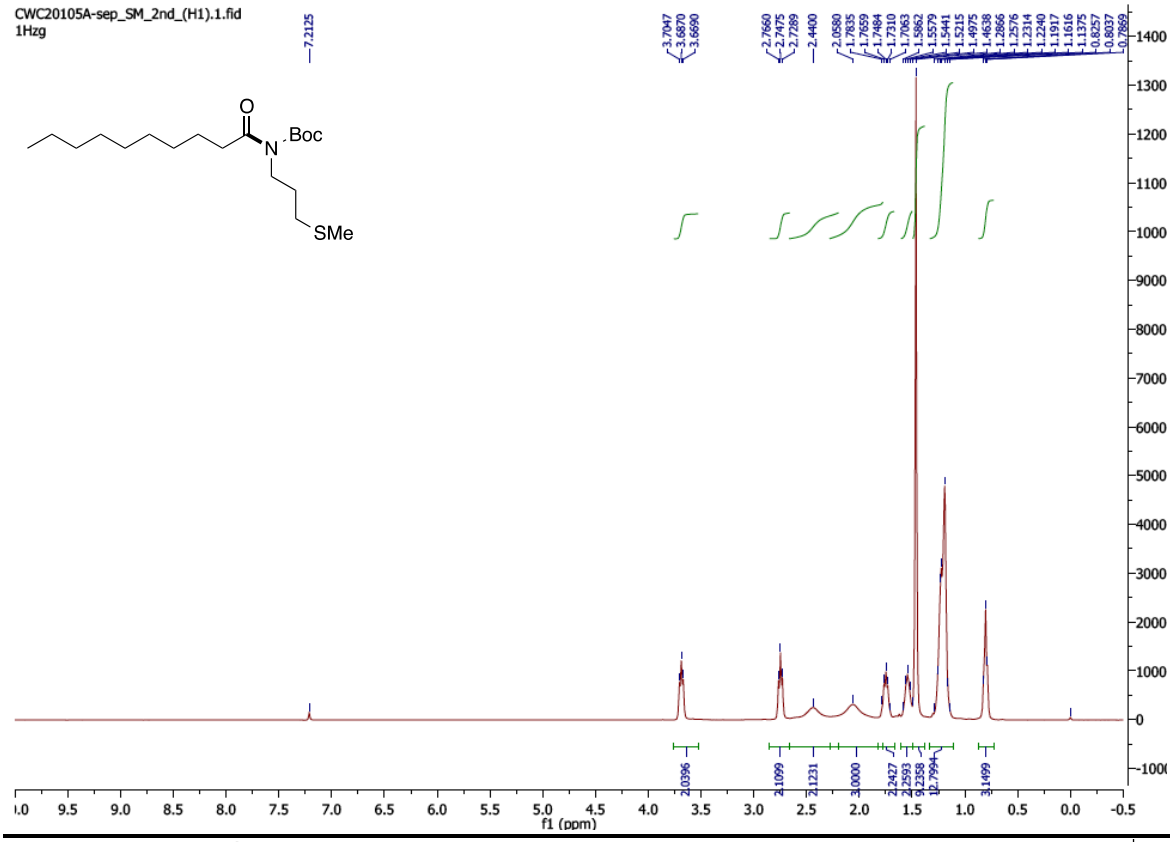


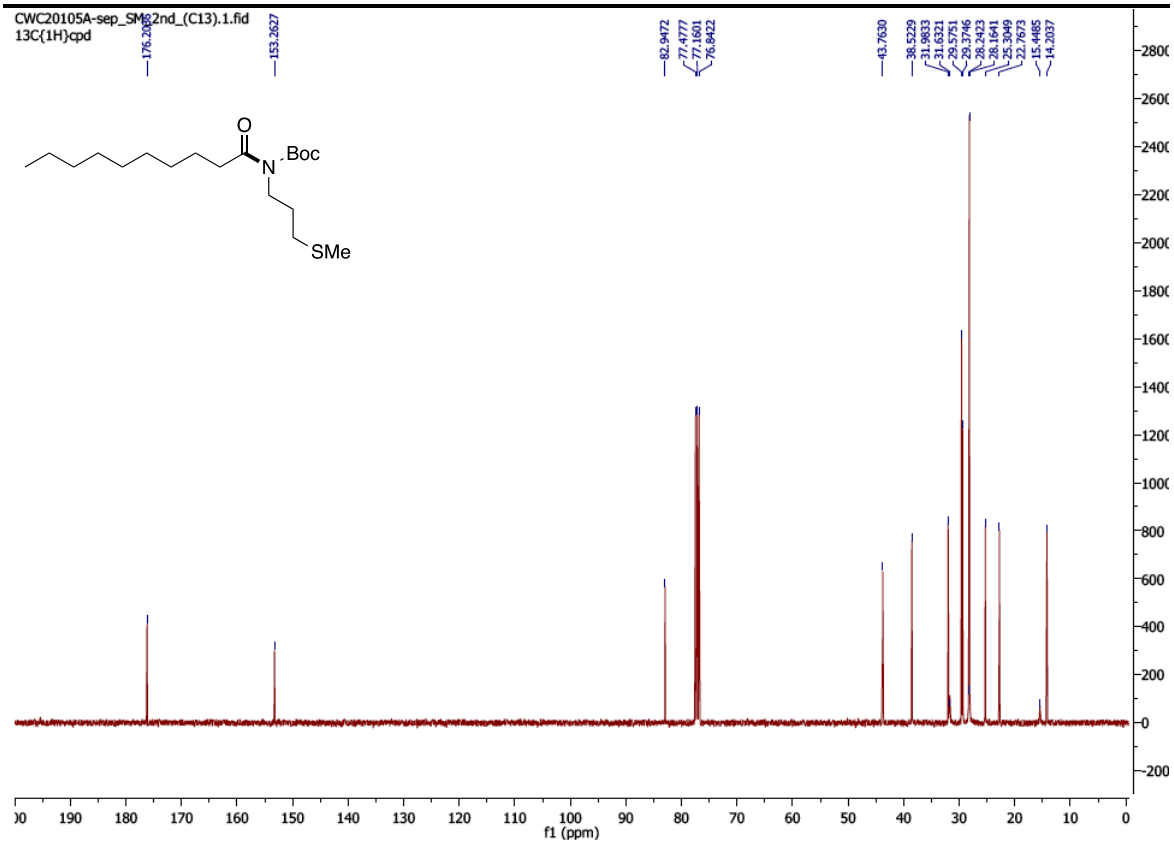
^{1}H and ^{13}C NMR of *tert*-Butyl Decanoyl(2-methoxyethyl)carbamate (S9).



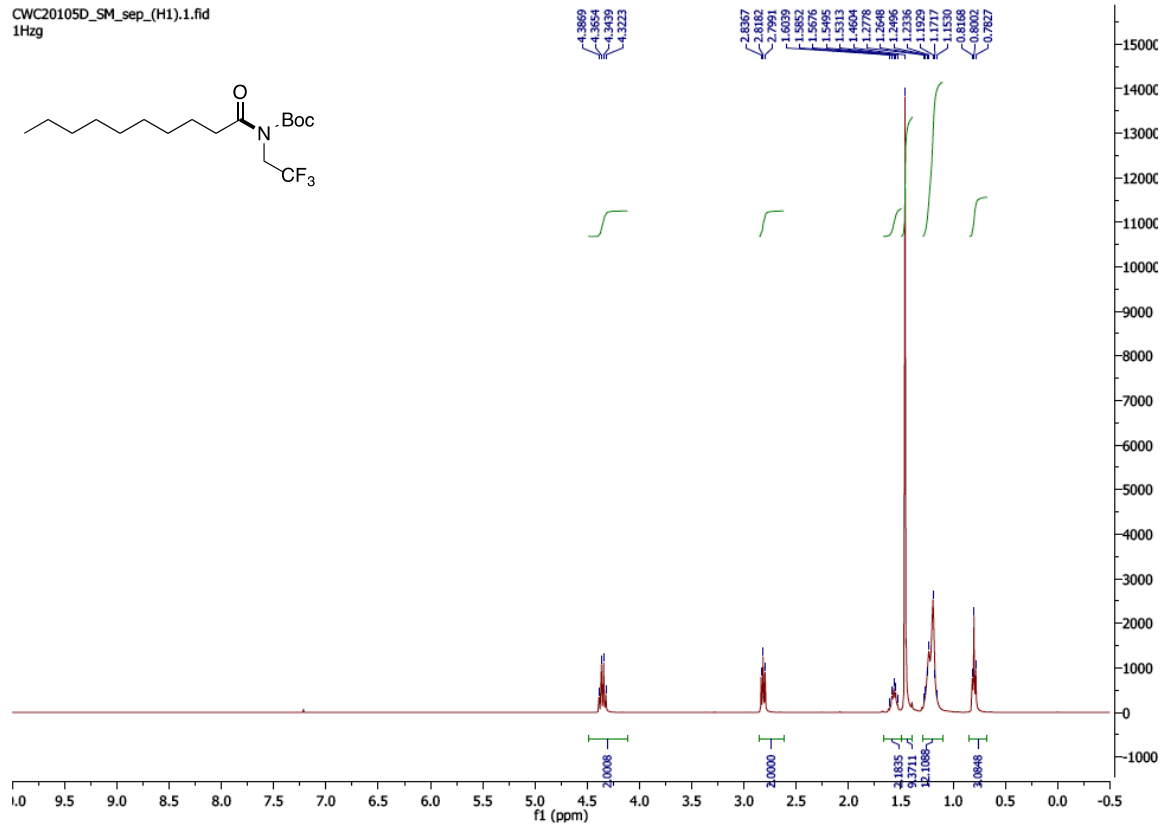


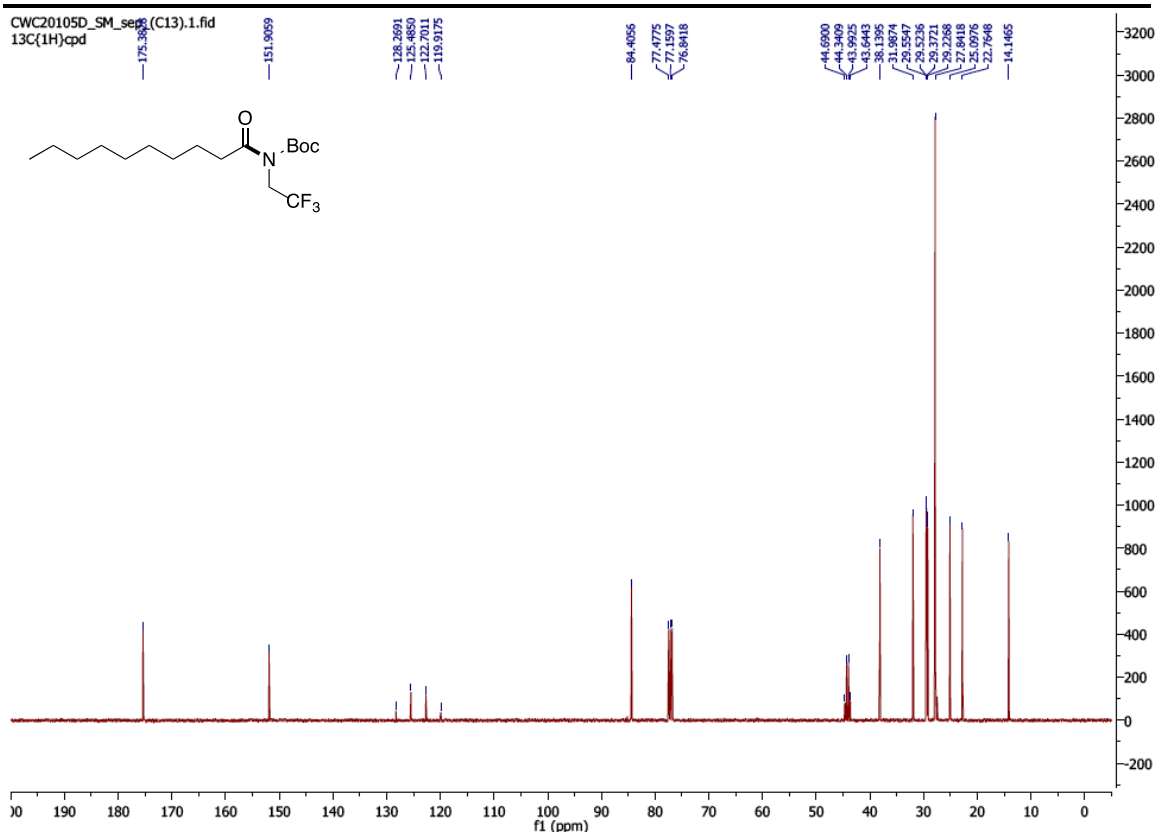
^{1}H and ^{13}C NMR of *tert*-Butyl Decanoyl(3-(methylthio)propyl)carbamate (S10).



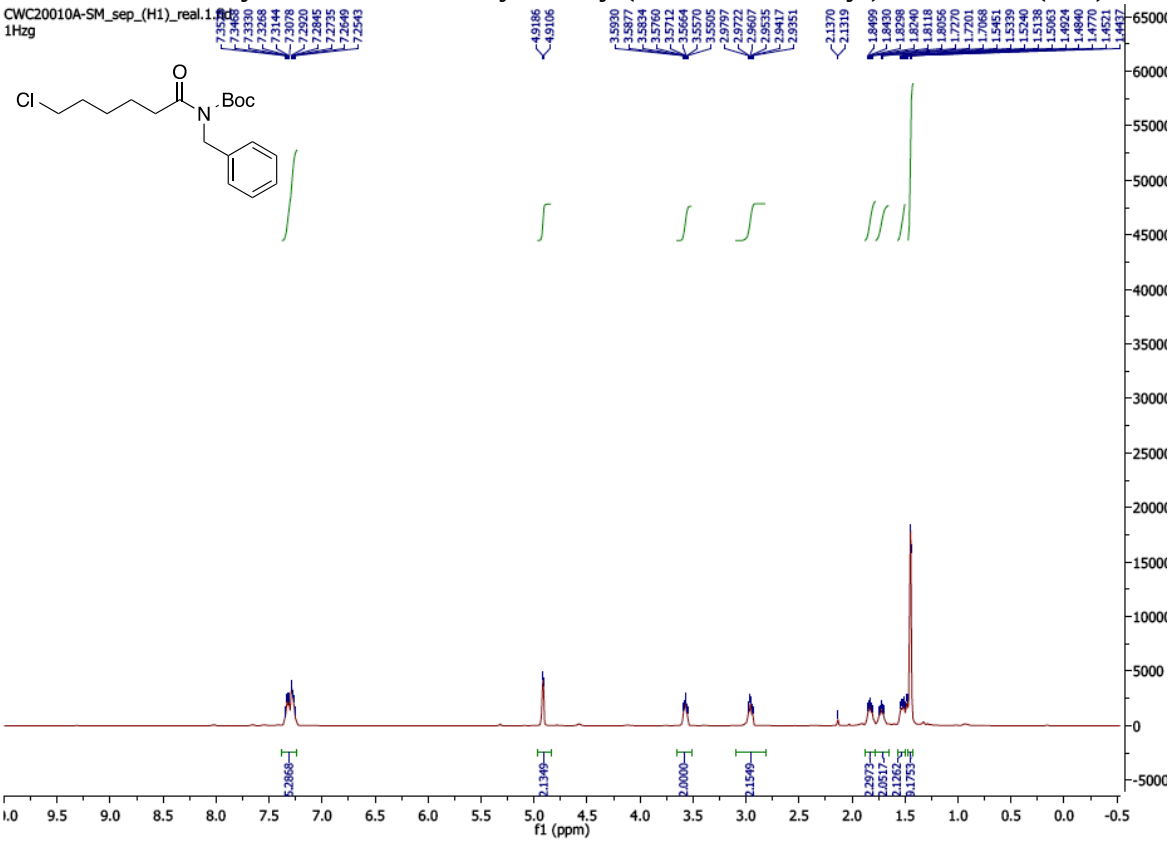


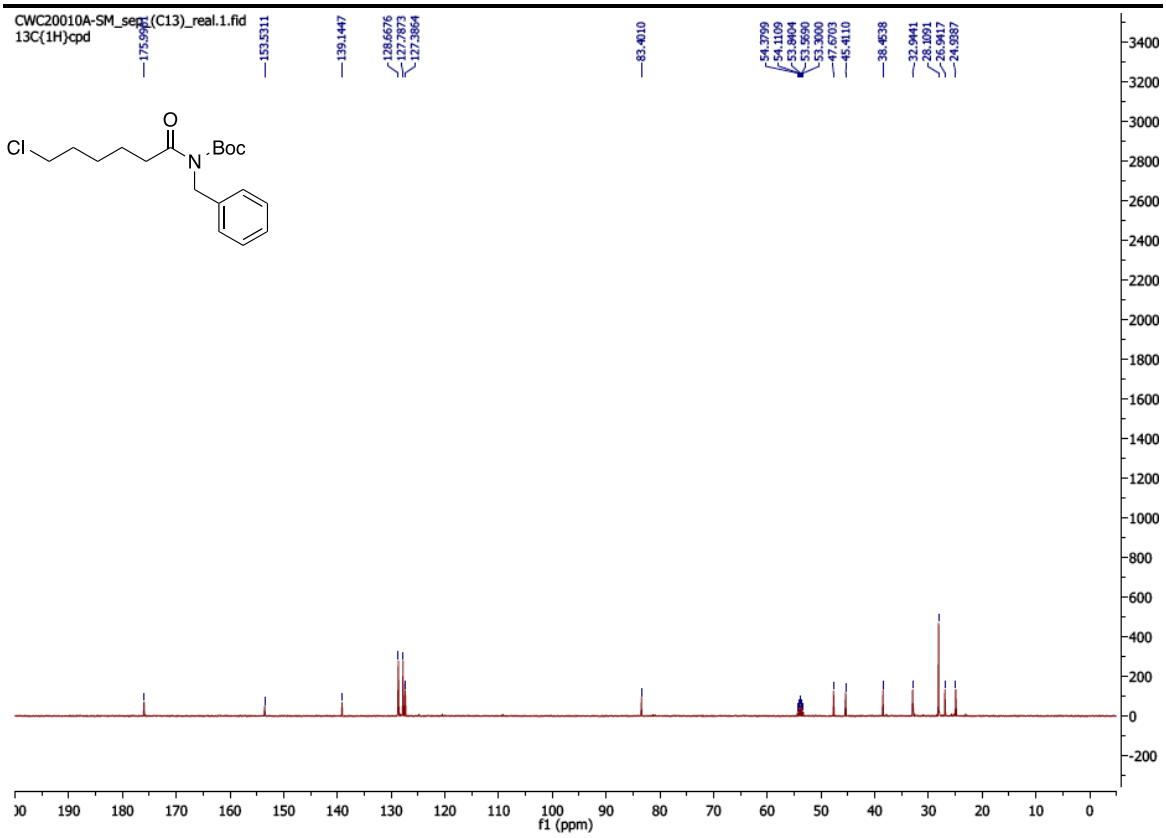
^{1}H and ^{13}C NMR of *tert*-Butyl Decanoyl(2,2,2-trifluoroethyl)carbamate (S11).



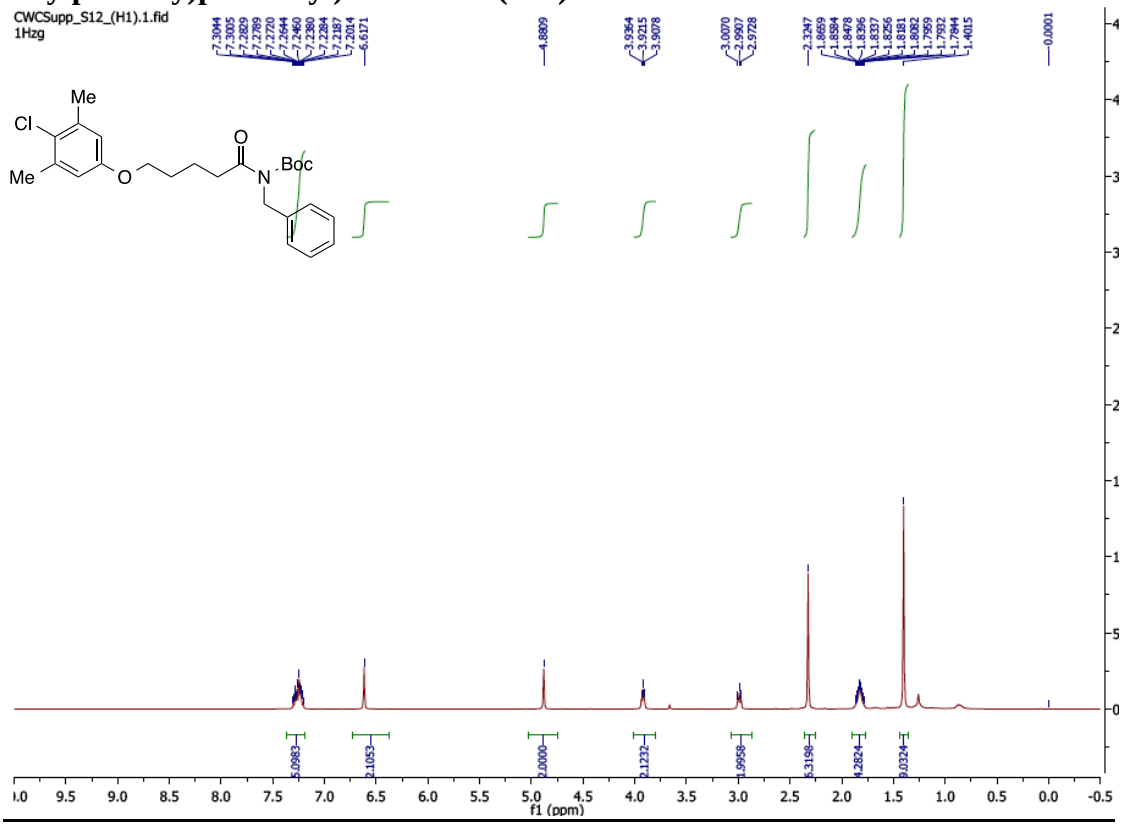


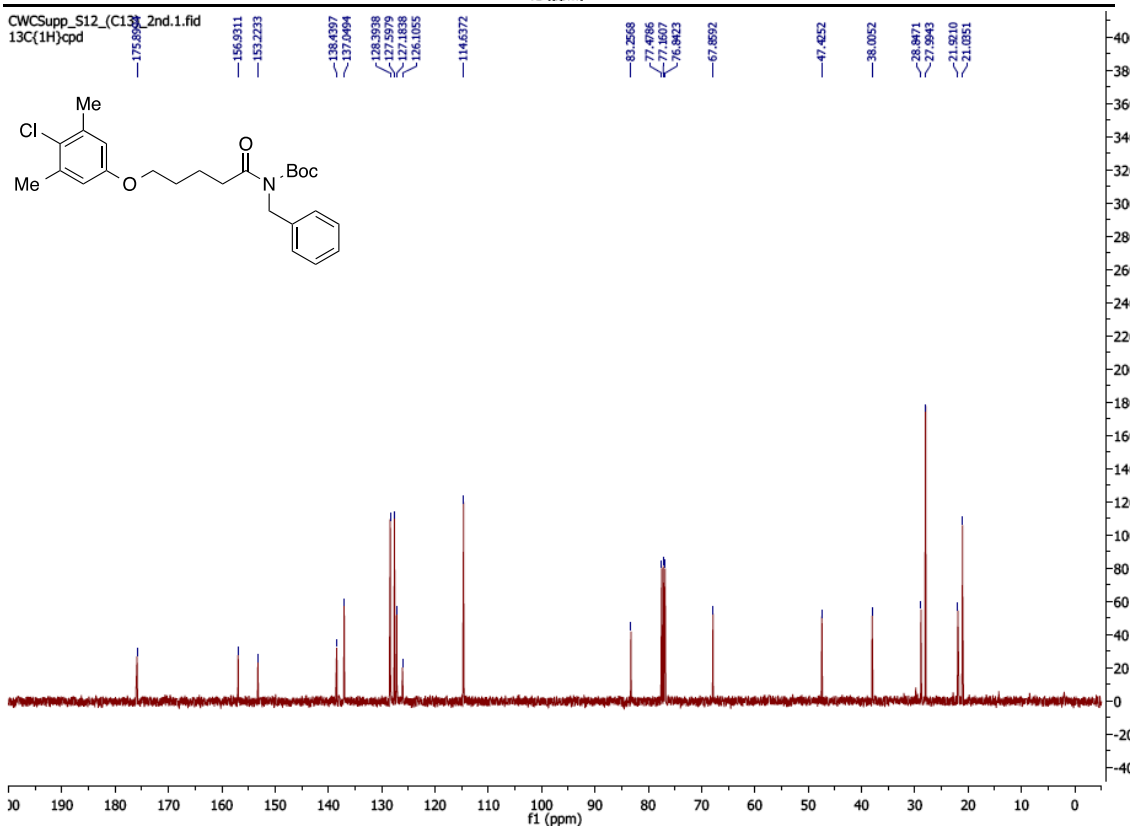
^{1}H and ^{13}C NMR of Synthesis of *tert*-Butyl Benzyl(6-chlorohexanoyl)carbamate (S12).



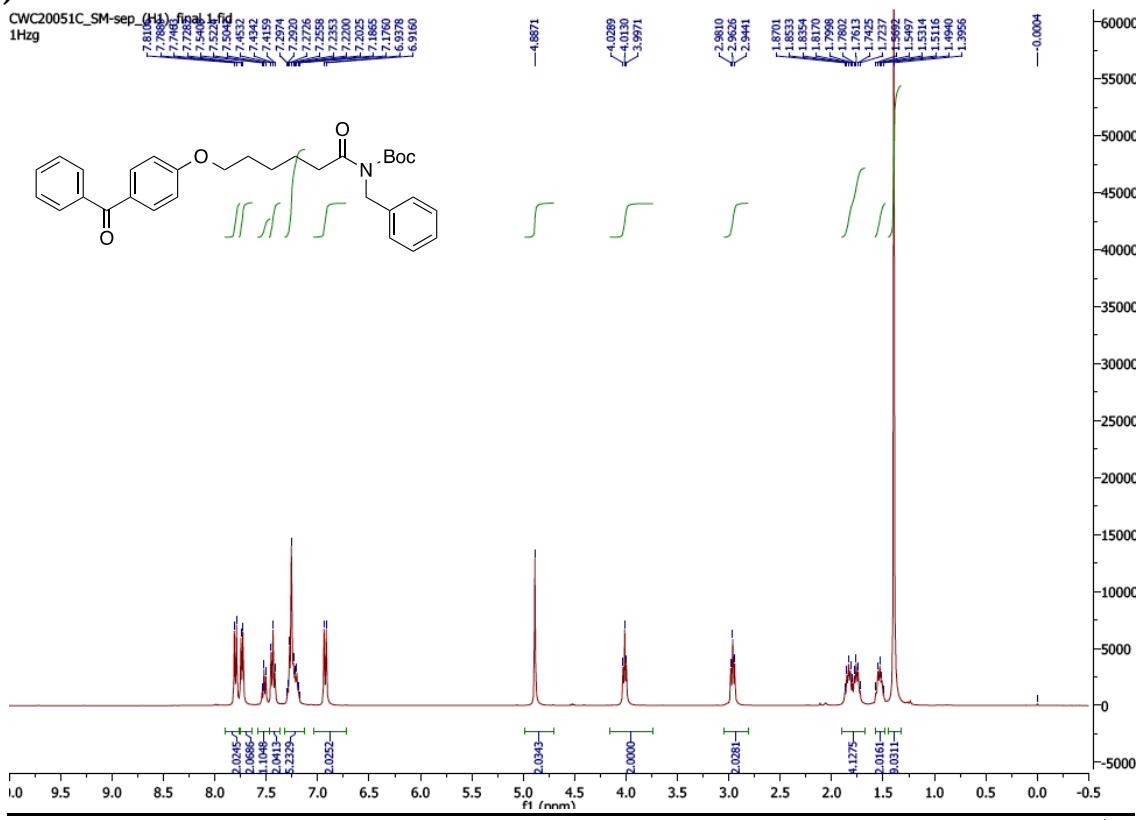


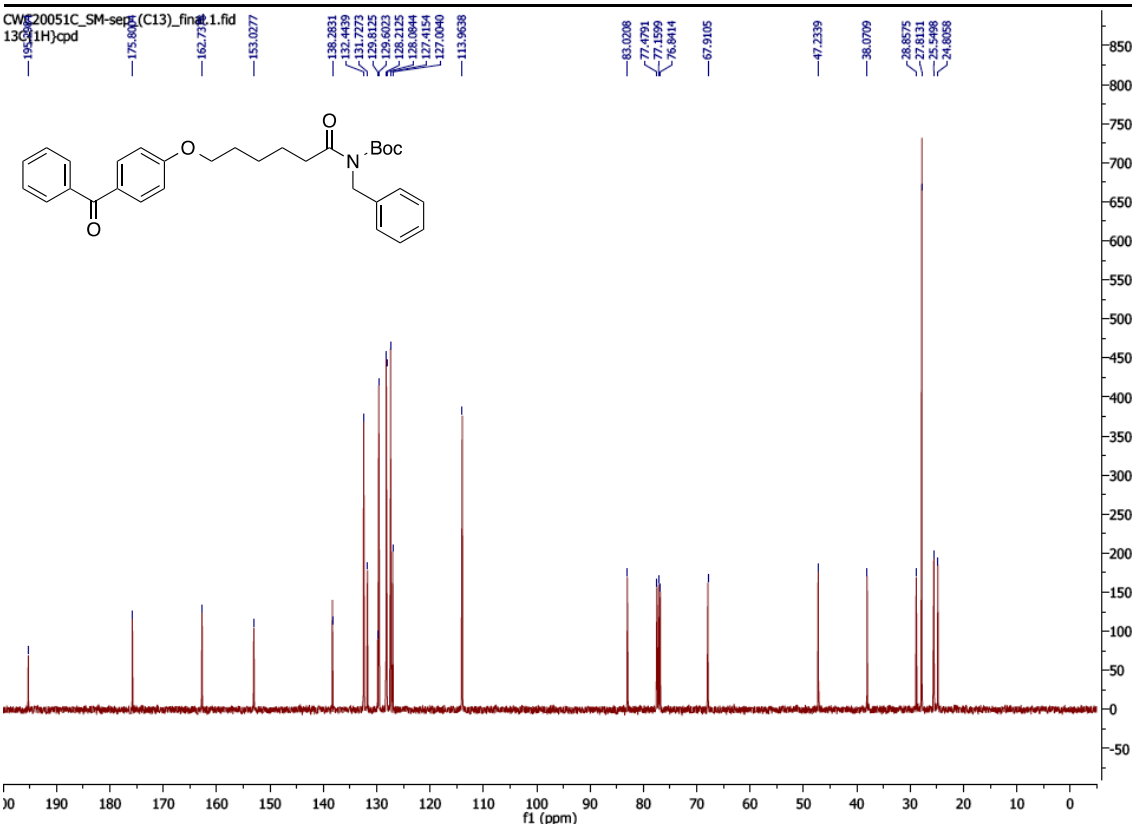
^{1}H and ^{13}C NMR of Synthesis of *tert*-Butyl Benzyl(5-(4-chloro-3,5-dimethylphenoxy)pentanoyl)carbamate (S13).



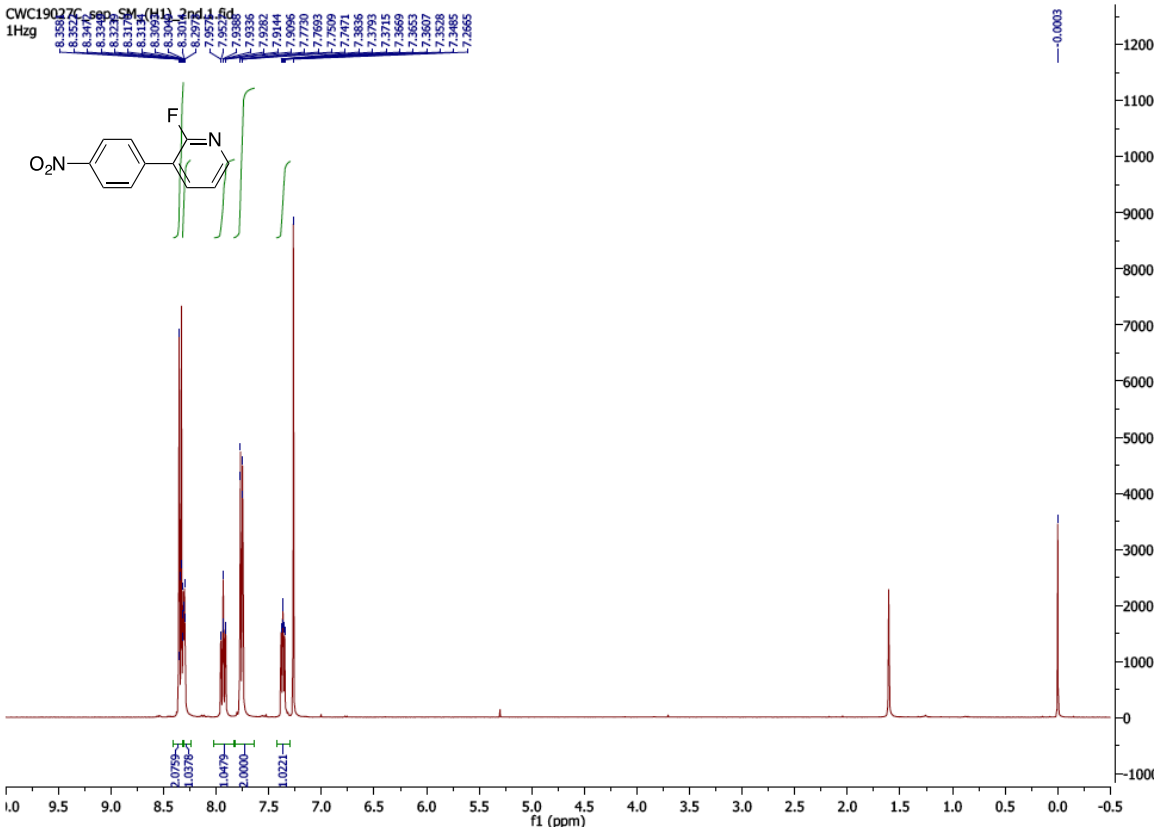


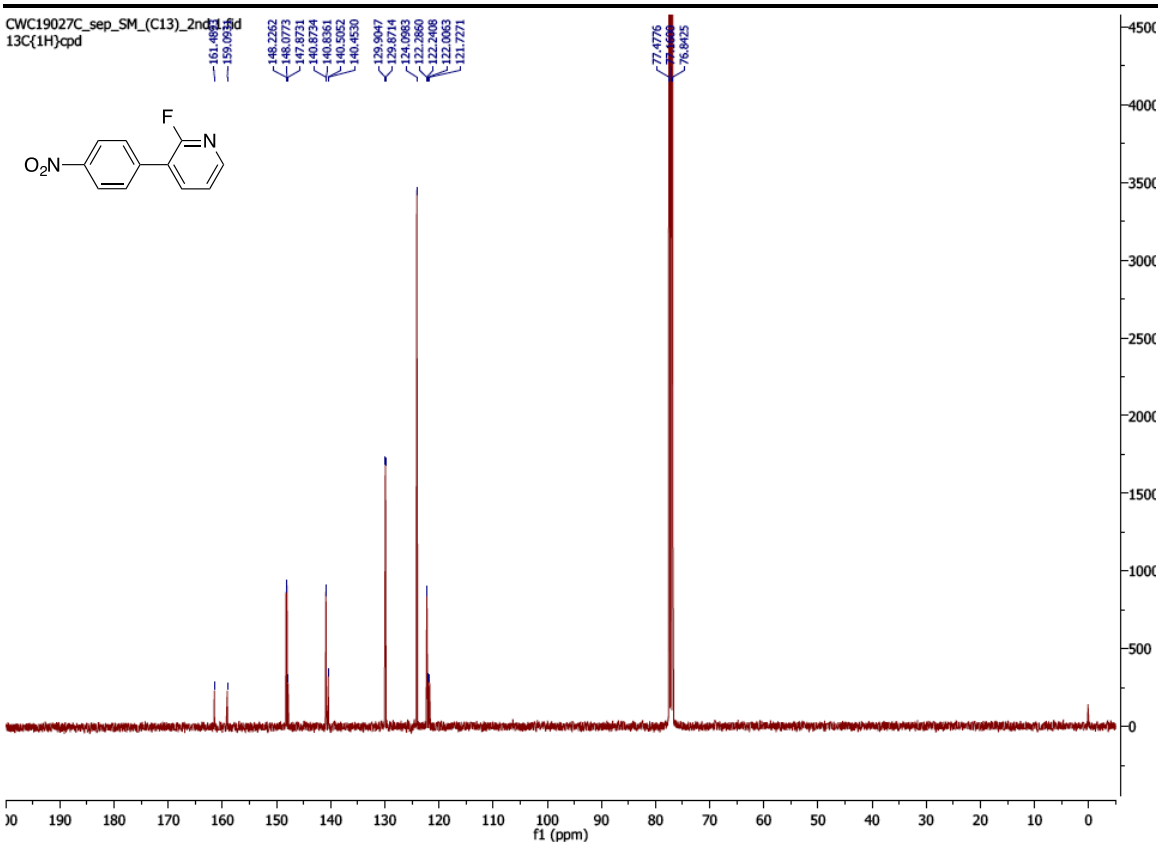
^{1}H and ^{13}C NMR of Synthesis of *tert*-Butyl (6-(4-Benzoylphenoxy)hexanoyl)(benzyl)carbamate (S14).



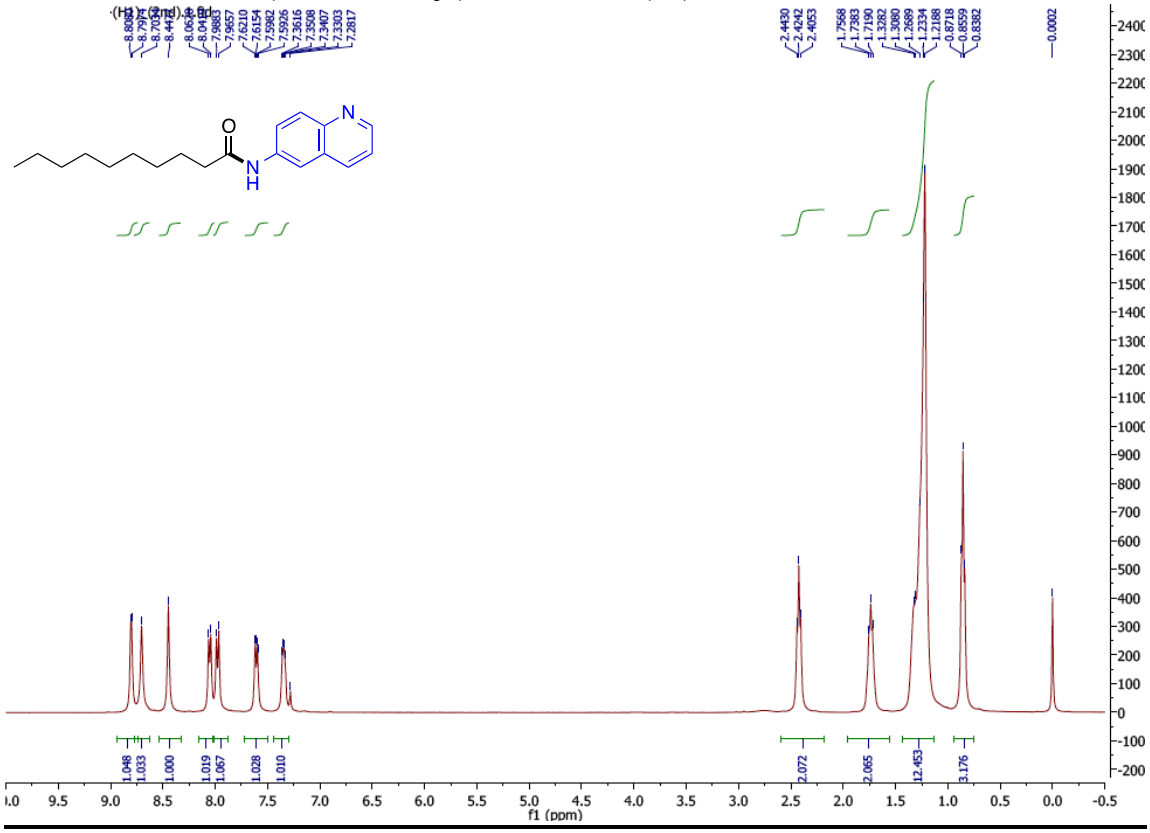


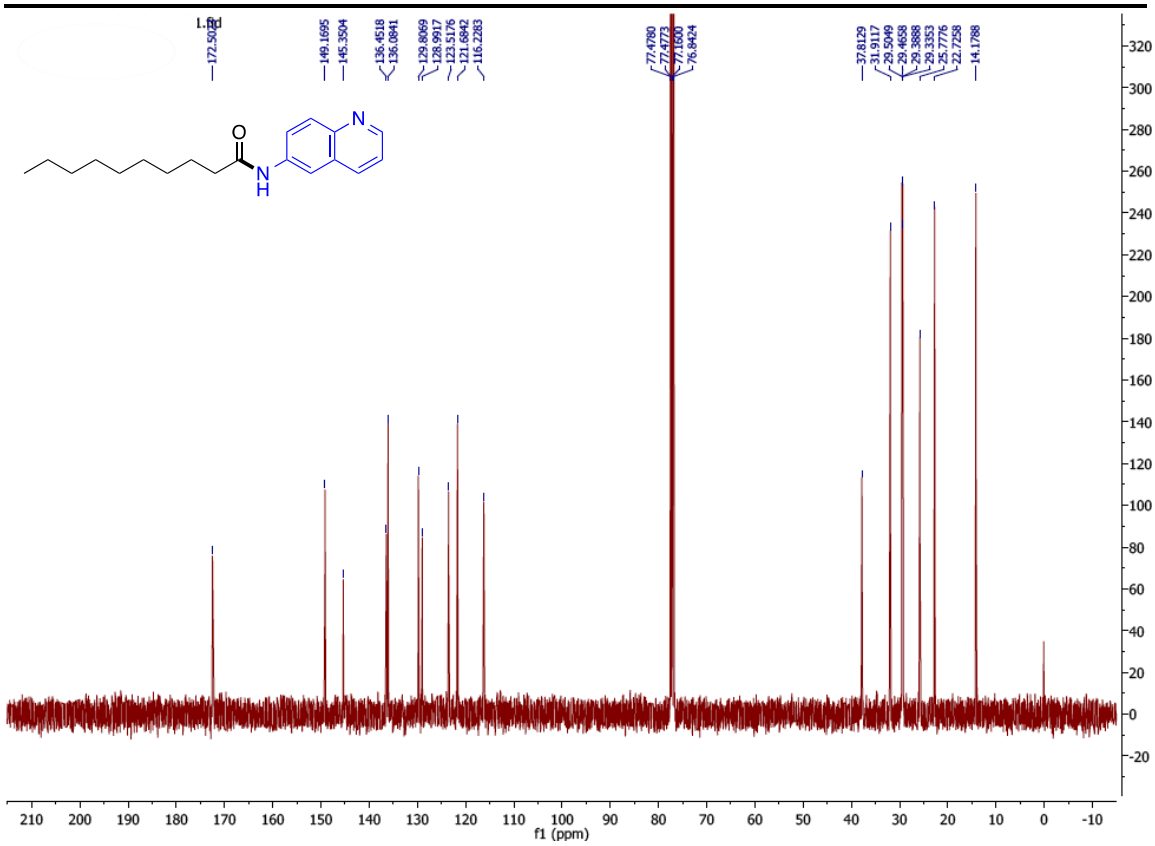
^{1}H and ^{13}C NMR of 2-Fluoro-3-(4-nitrophenyl)pyridine (S15).



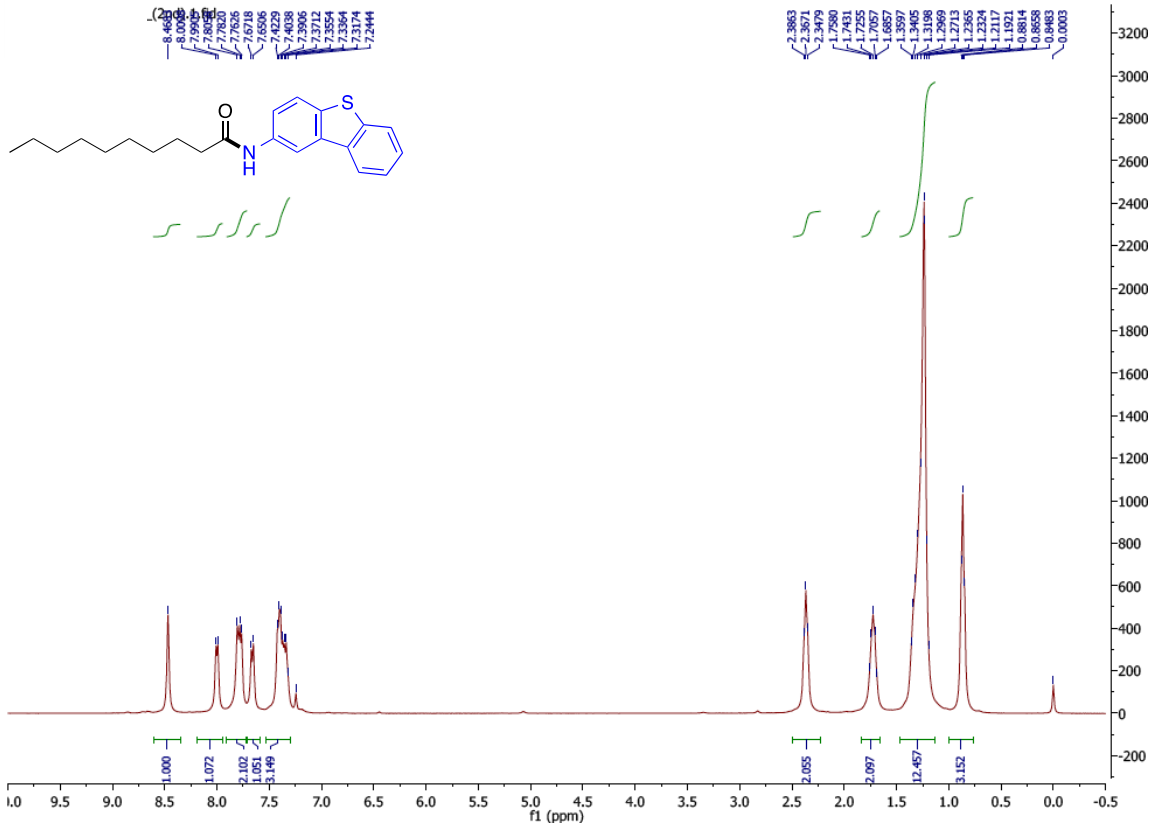


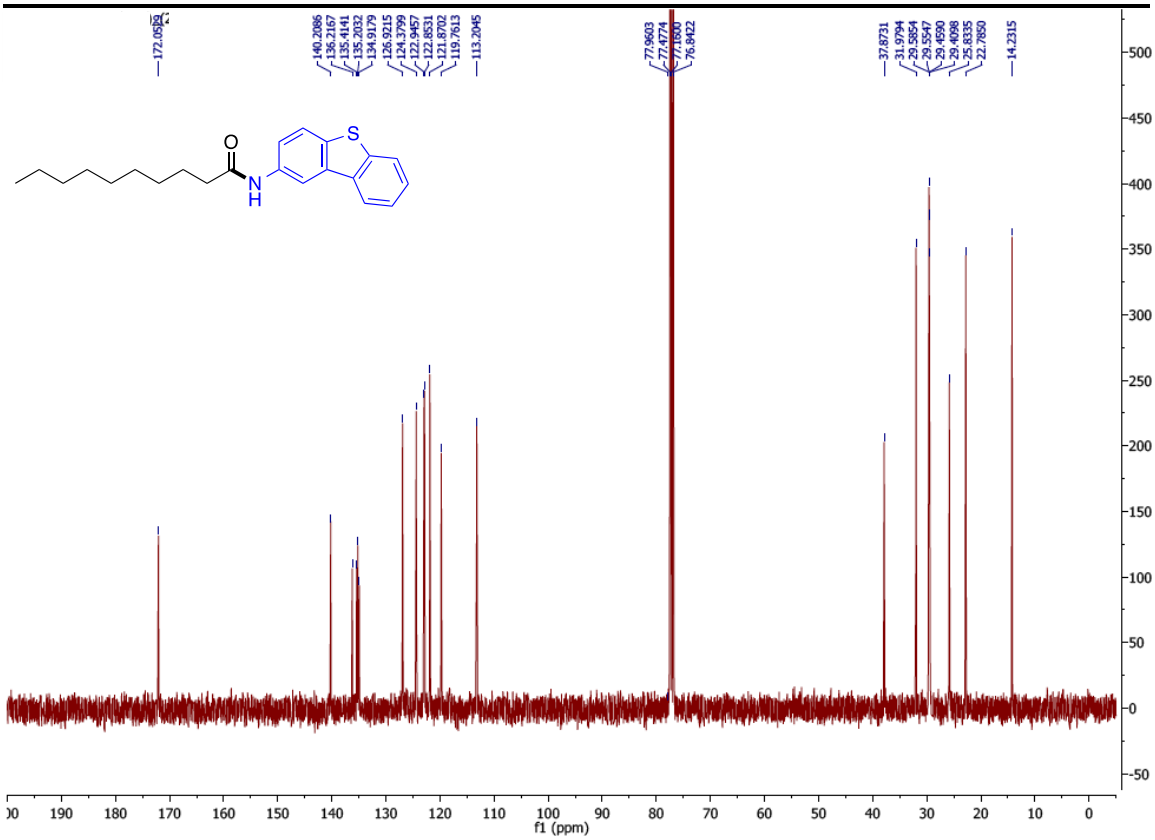
^{1}H and ^{13}C NMR of *N*-(Quinolin-6-yl)decanamide (3a).



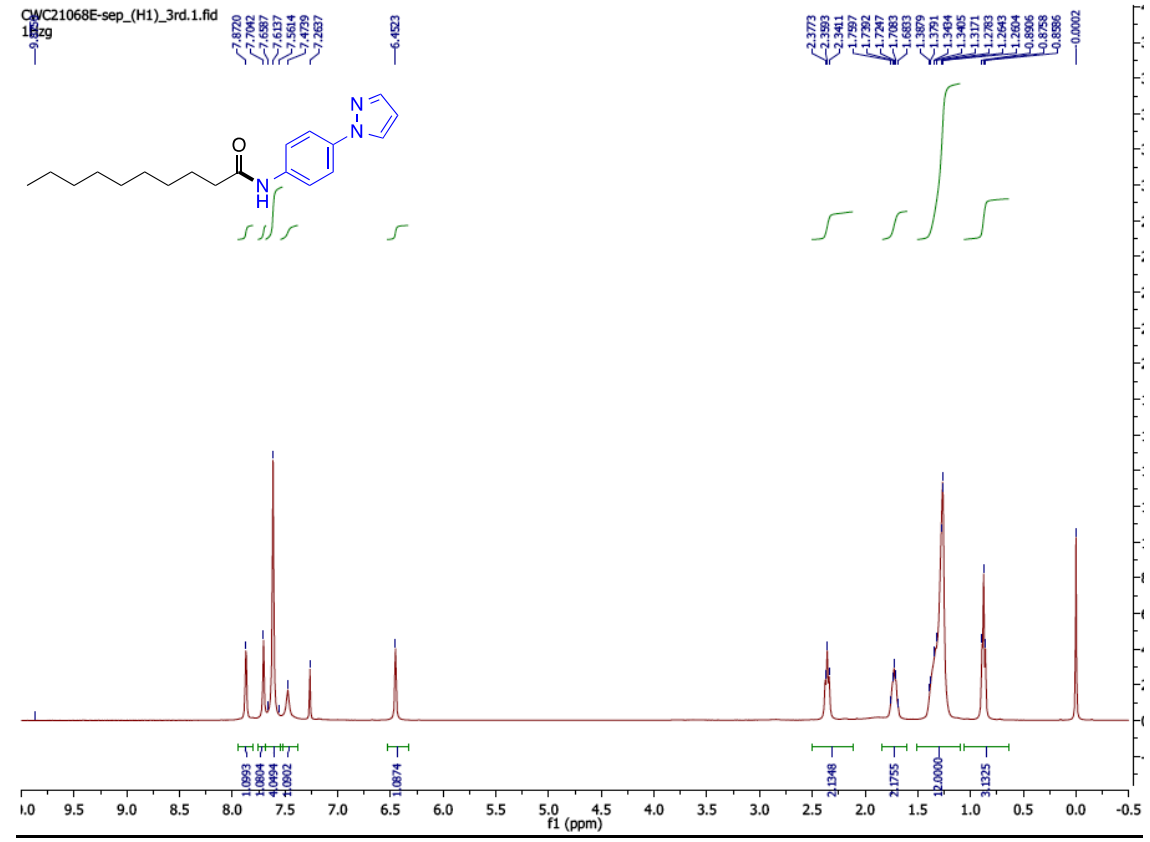


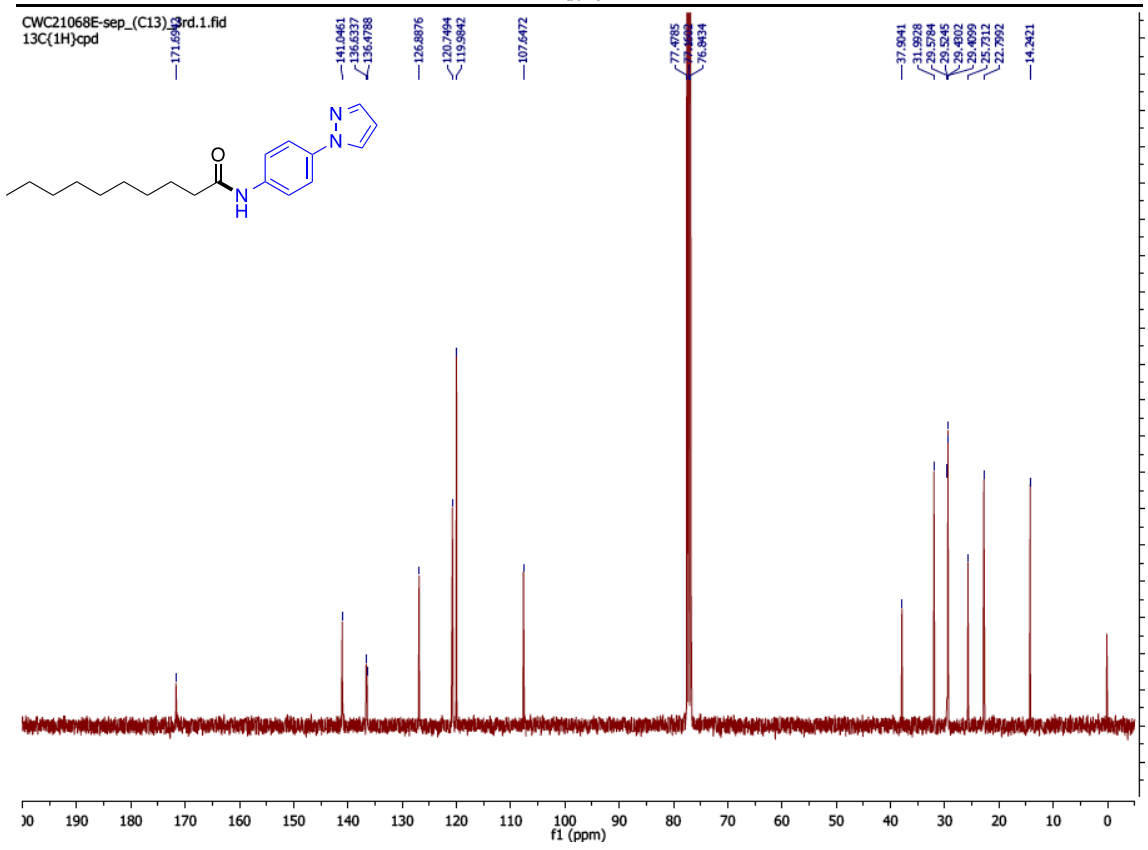
^{1}H and ^{13}C NMR of *N*-(Dibenzo[*b*,*d*]thiophen-3-yl)decanamide (3b).



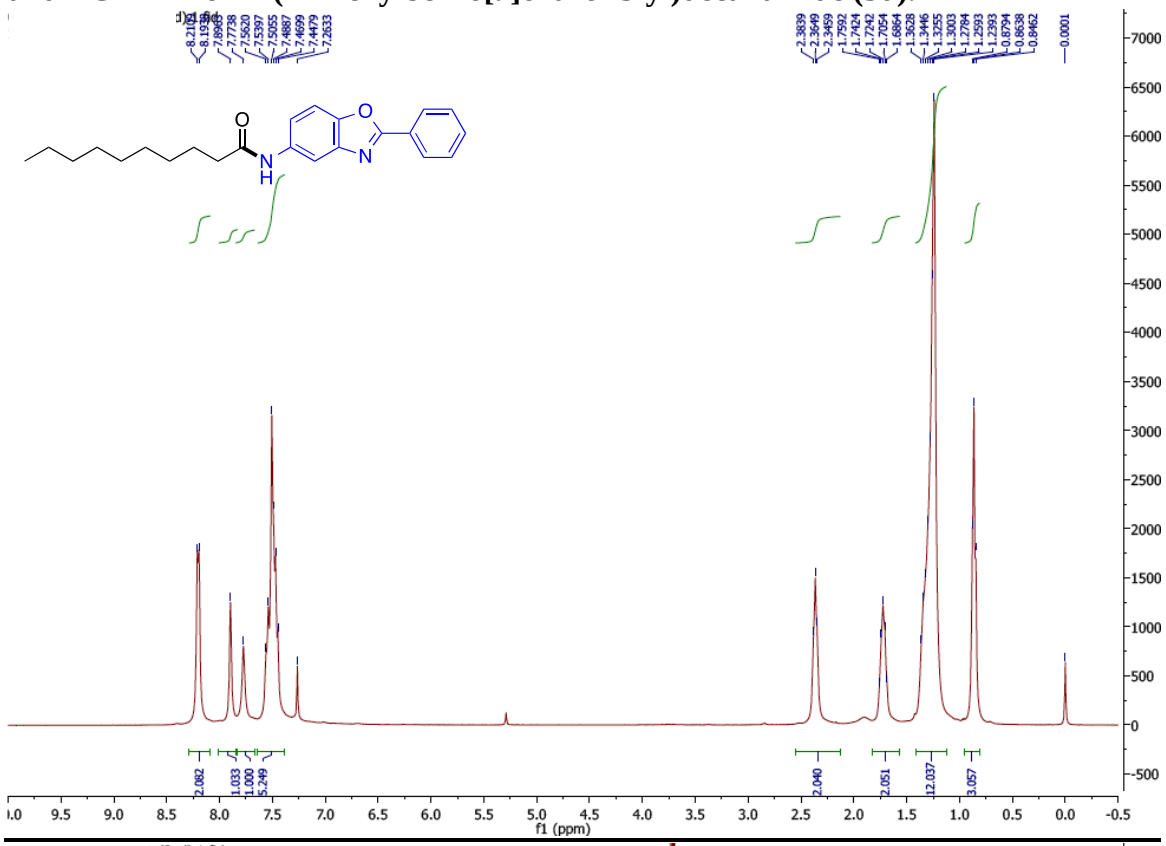


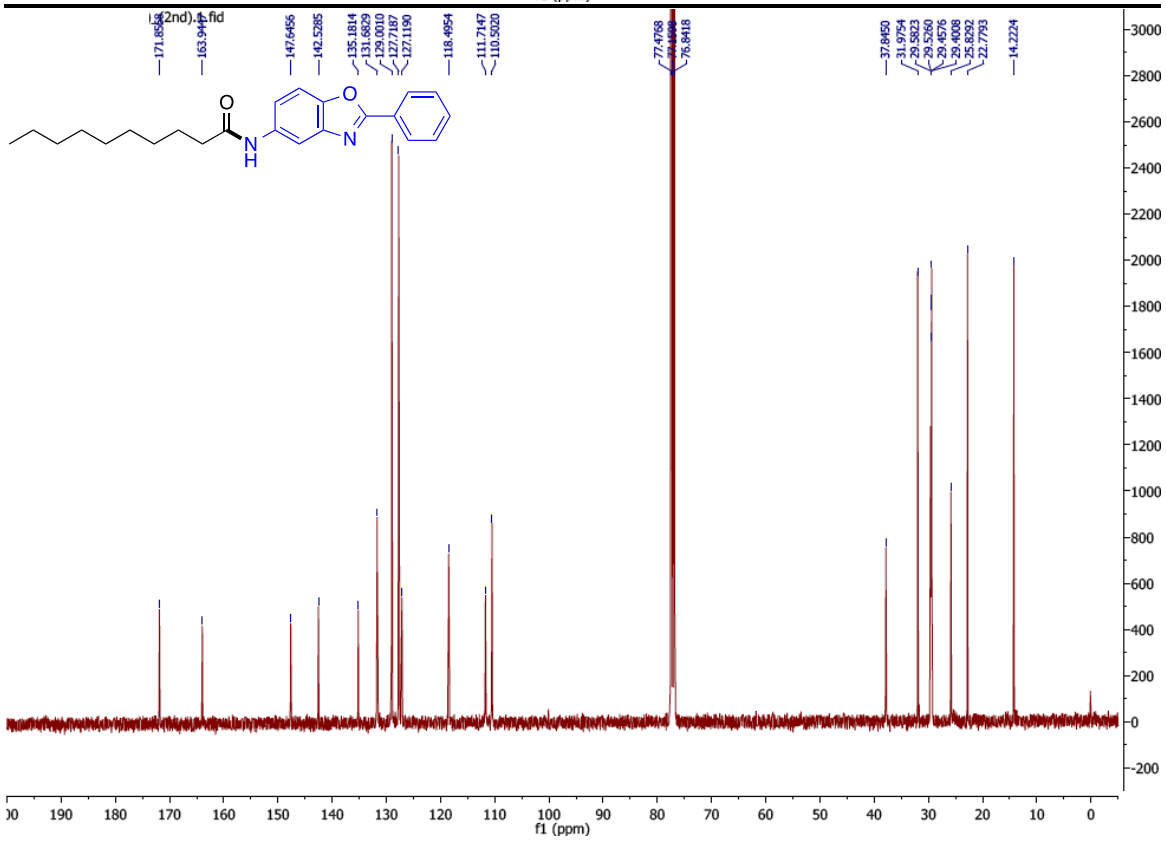
^{1}H and ^{13}C NMR of *N*-(4-(1*H*-Pyrazol-1-yl)phenyl)decanamide (3c).



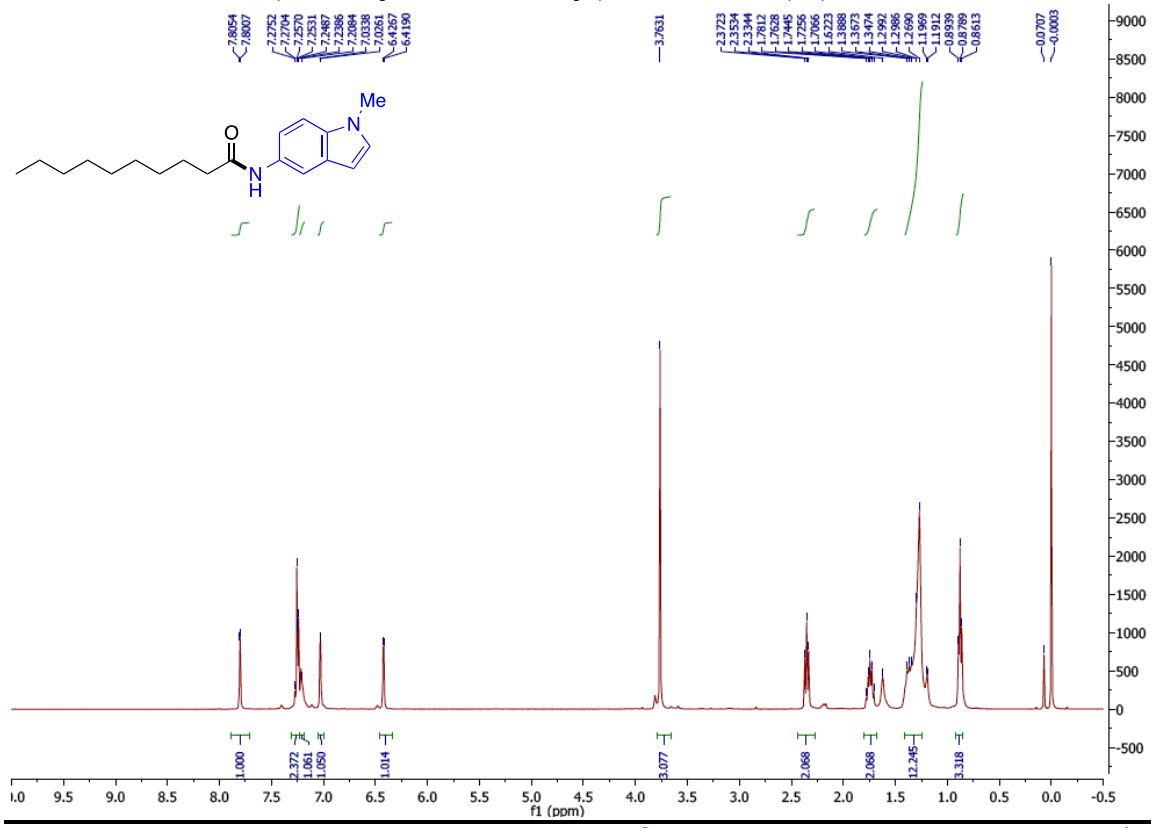


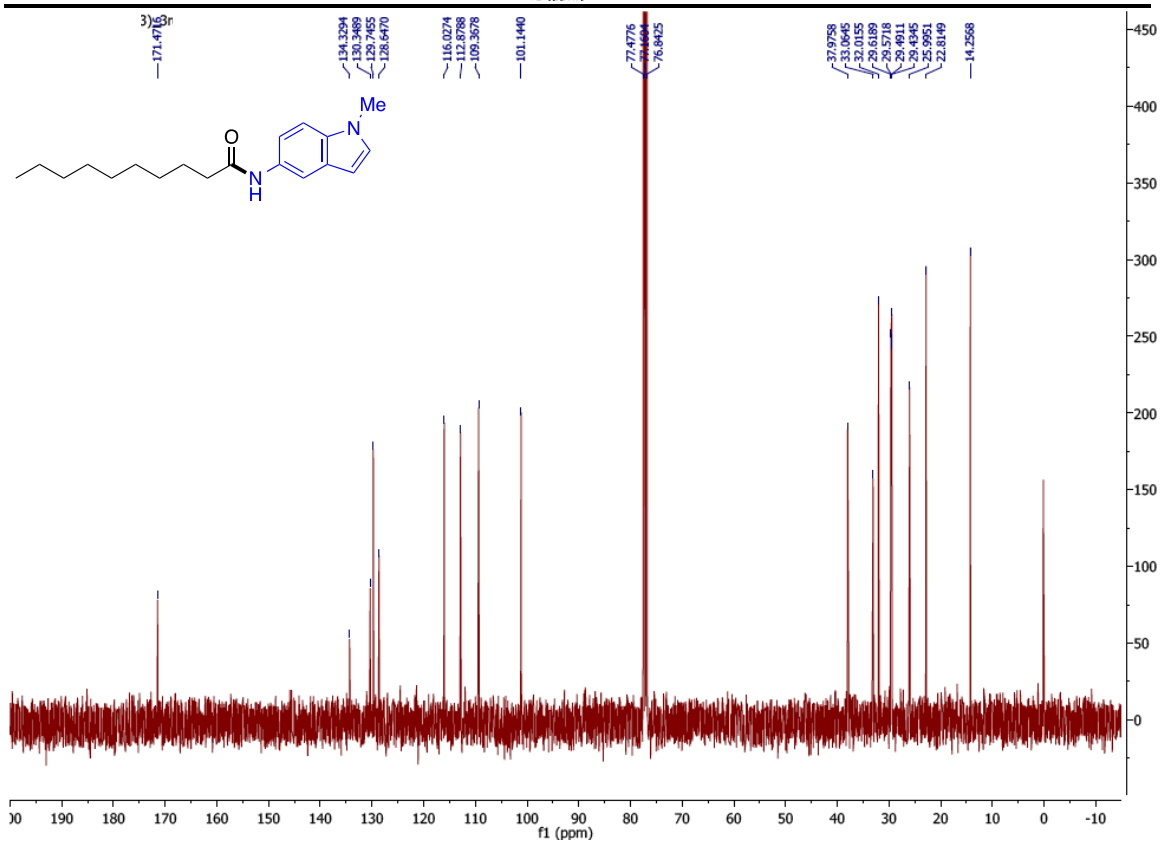
^{1}H and ^{13}C NMR of *N*-(2-Phenylbenzo[*d*]oxazol-5-yl)decanamide (3d).



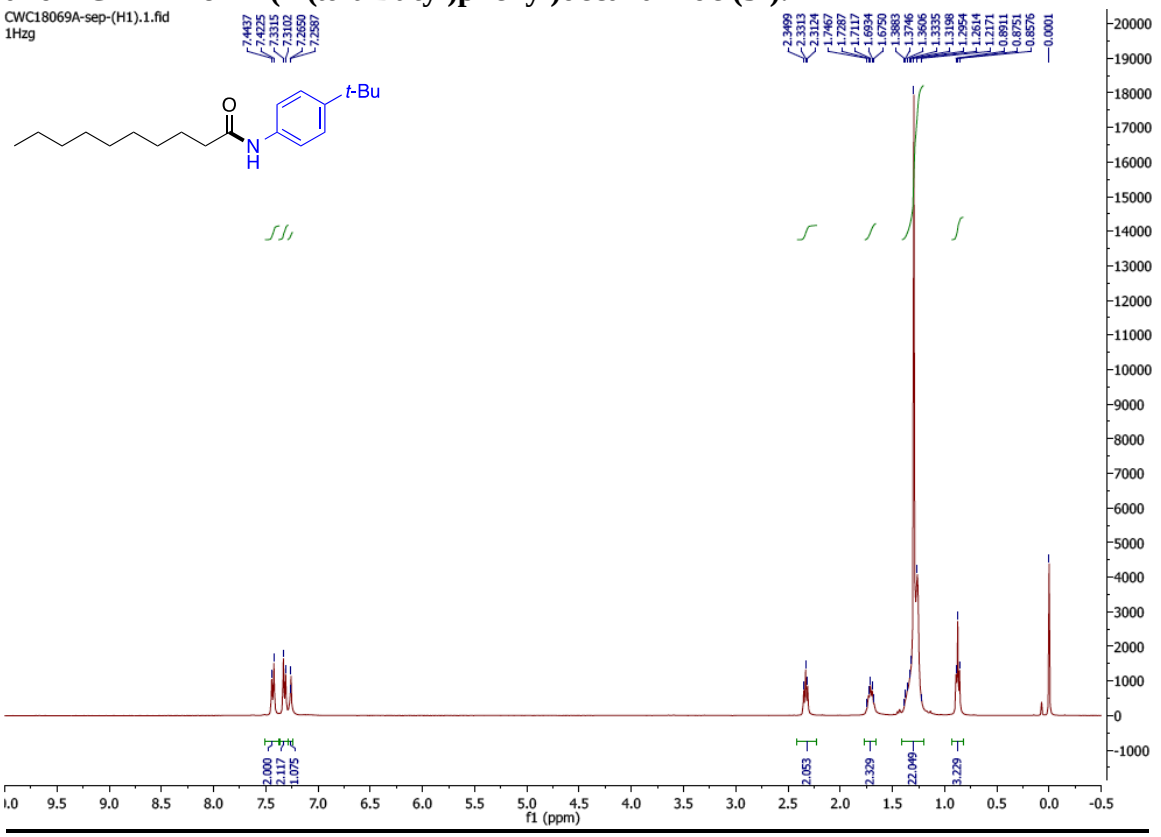


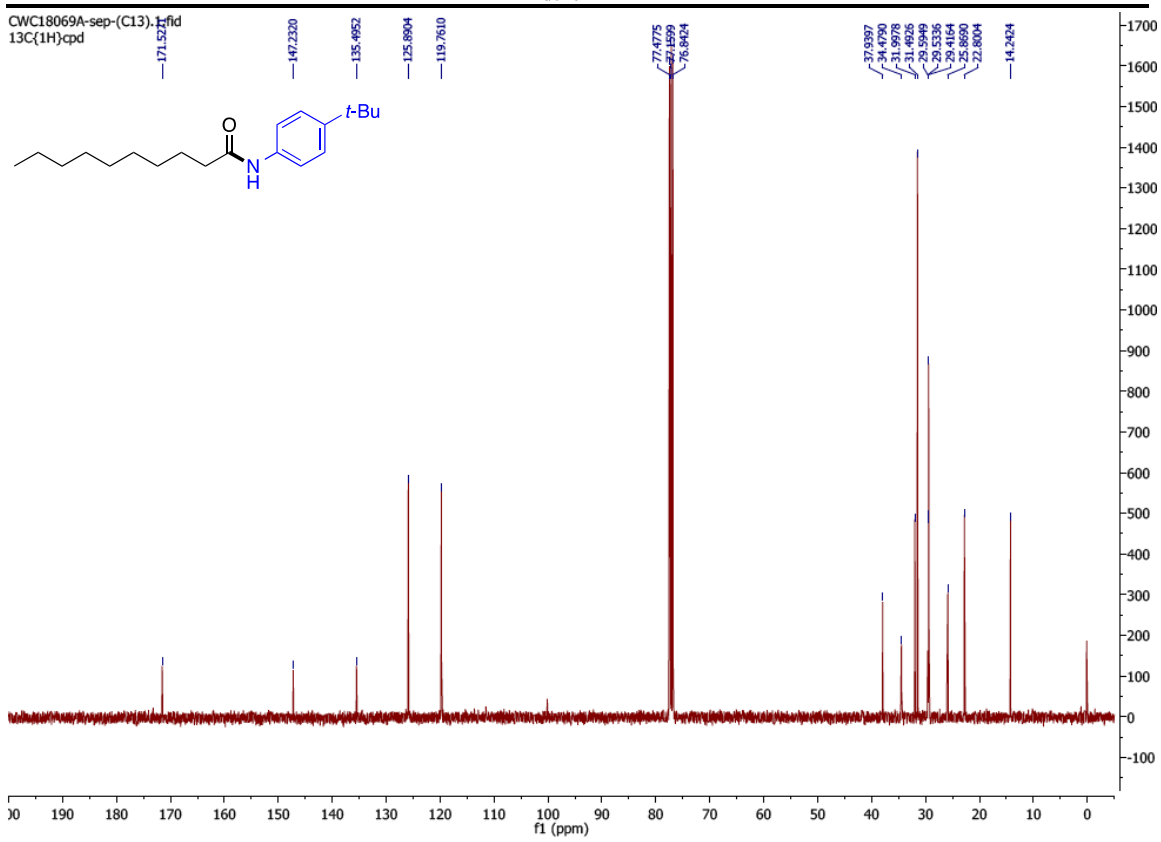
^{1}H and ^{13}C NMR of *N*-(1-Methyl-1*H*-indol-5-yl)decanamide (3e).



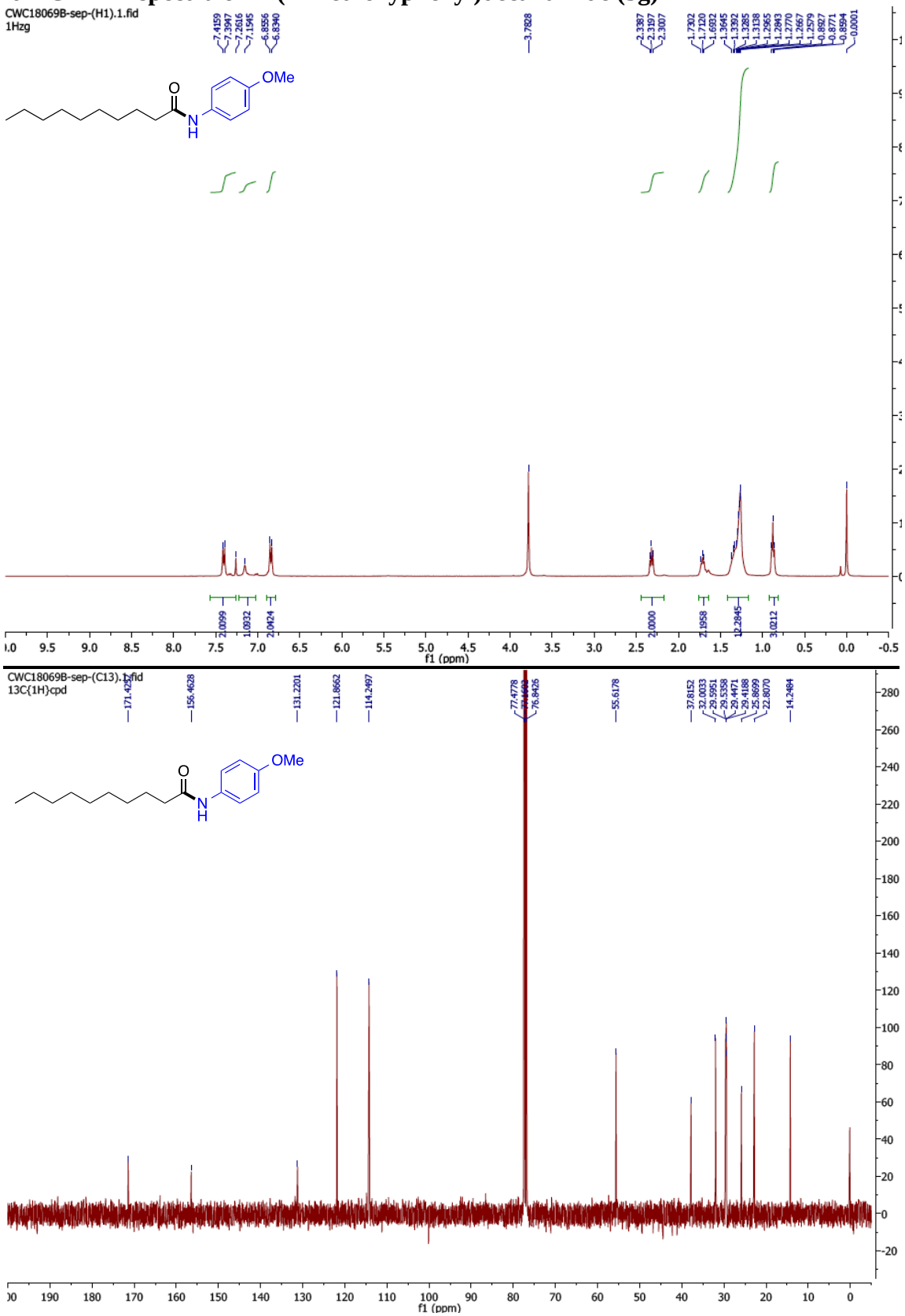


^{1}H and ^{13}C NMR of *N*-(4-(*tert*-Butyl)phenyl)decanamide (3f).

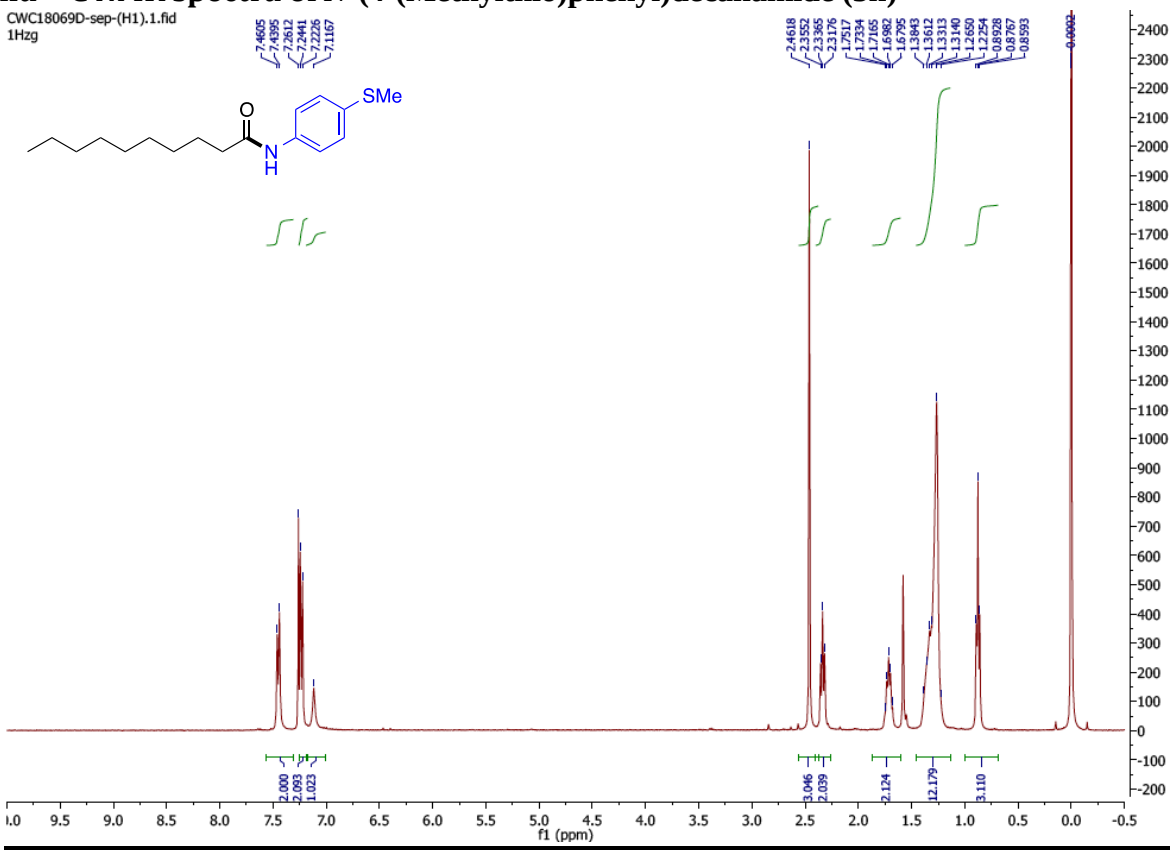


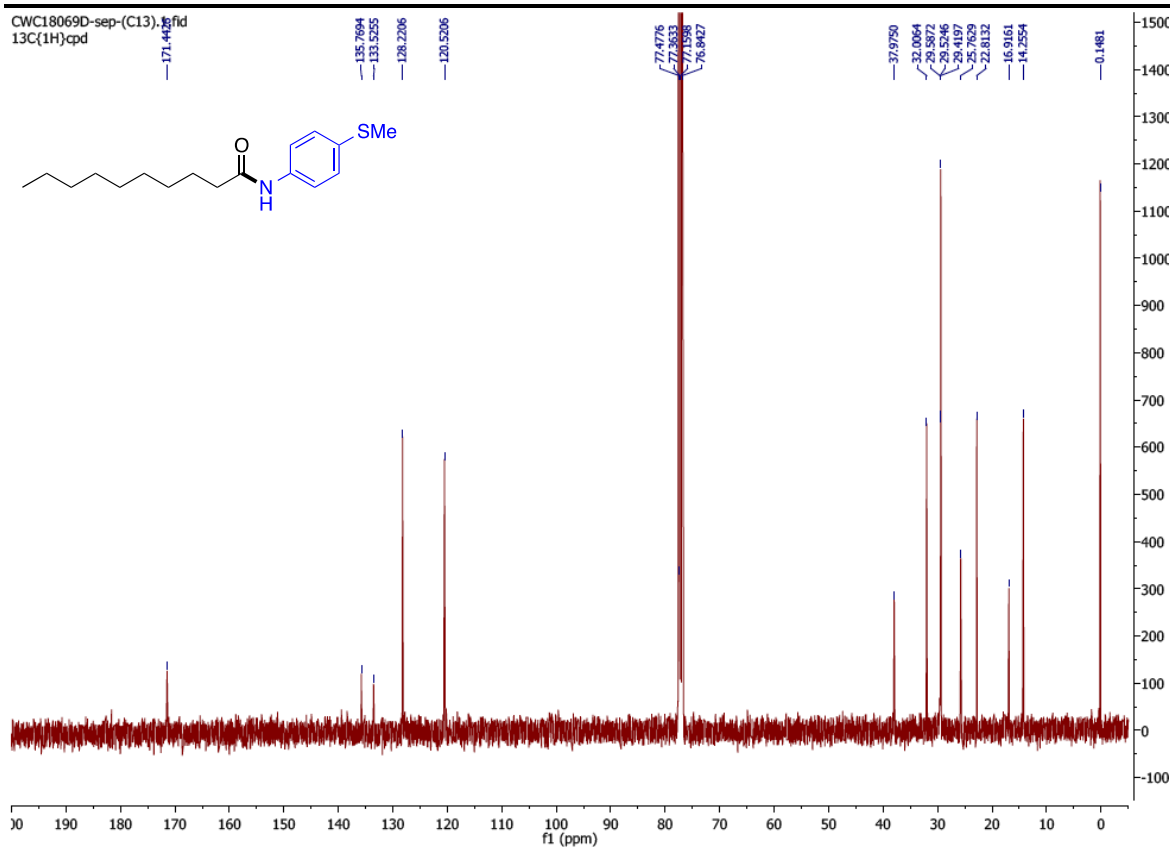


^{1}H and ^{13}C NMR spectra of *N*-(4-Methoxyphenyl)decanamide (3g)

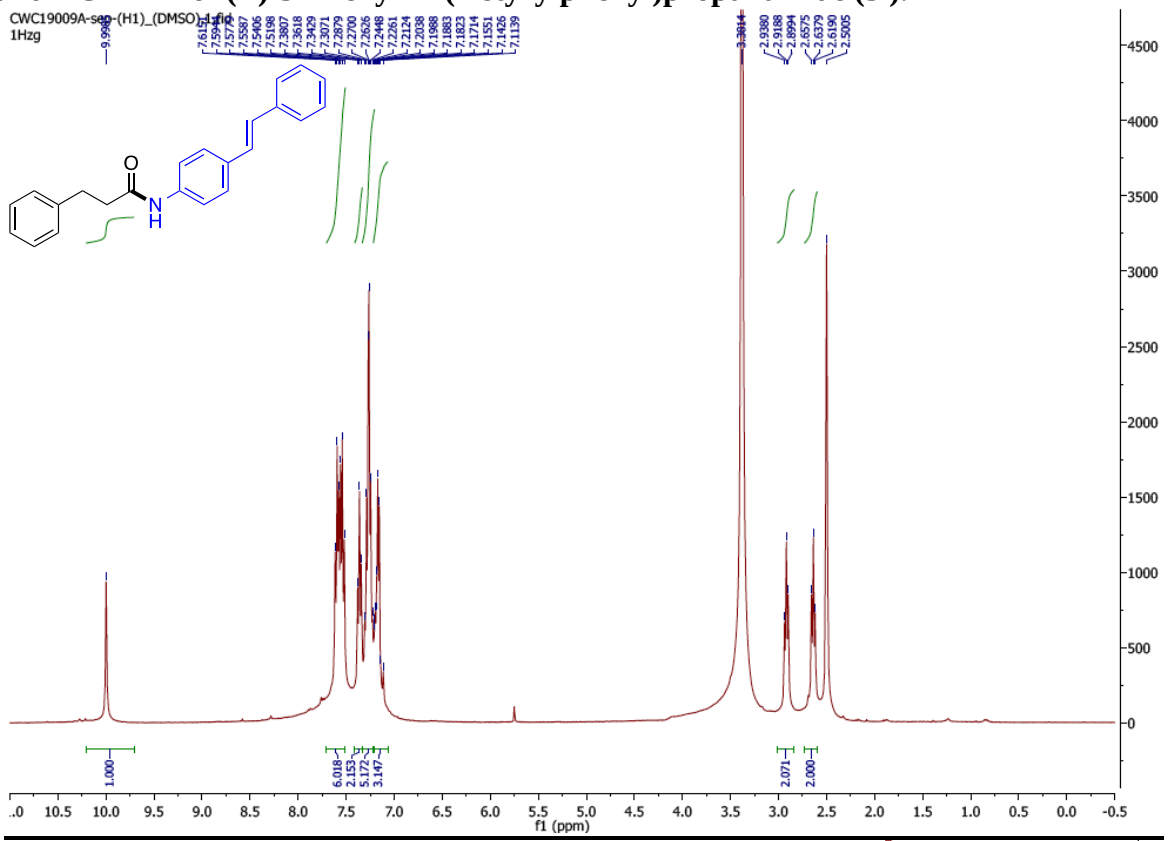


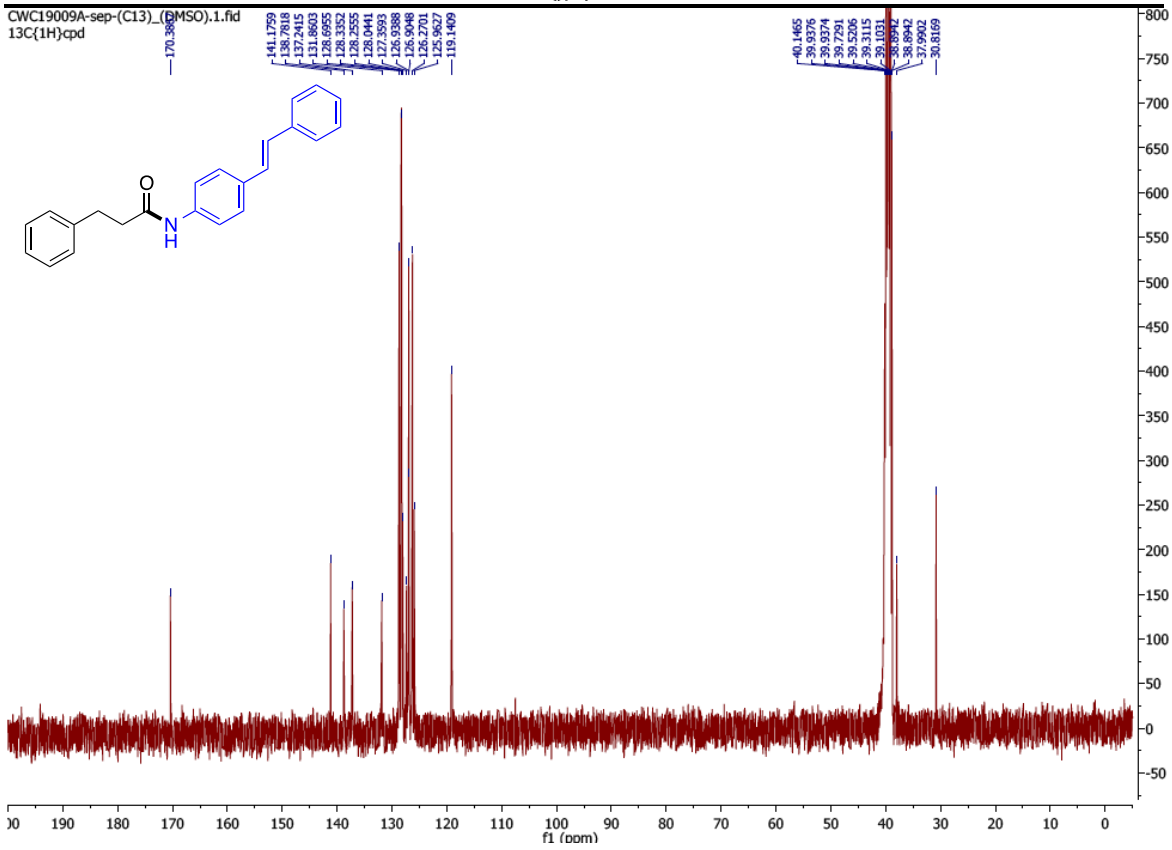
^{1}H and ^{13}C NMR spectra of *N*-(4-(Methylthio)phenyl)decanamide (3h)



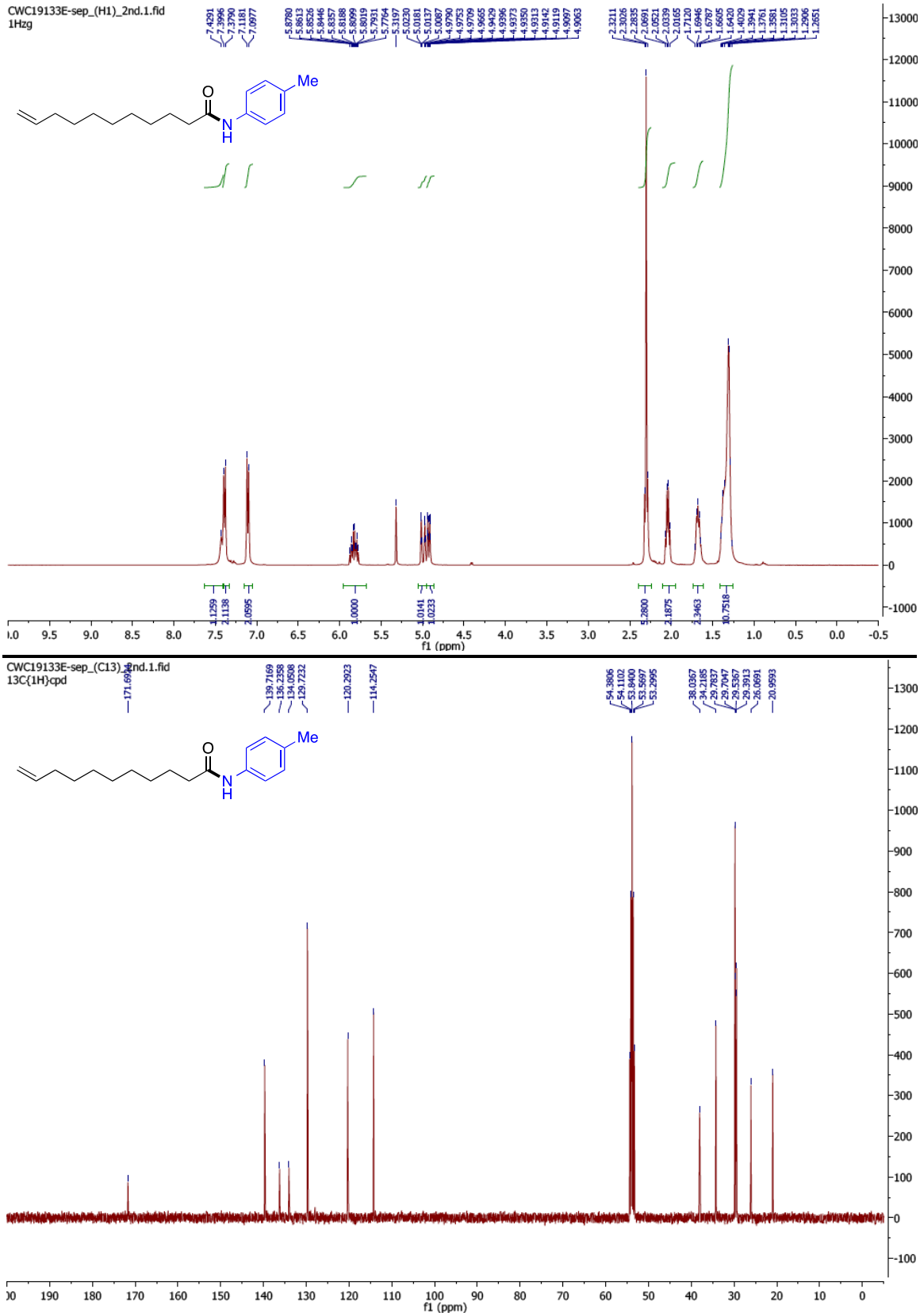


^{1}H and ^{13}C NMR of (*E*)-3-Phenyl-*N*-(4-styrylphenyl)propanamide (3i).

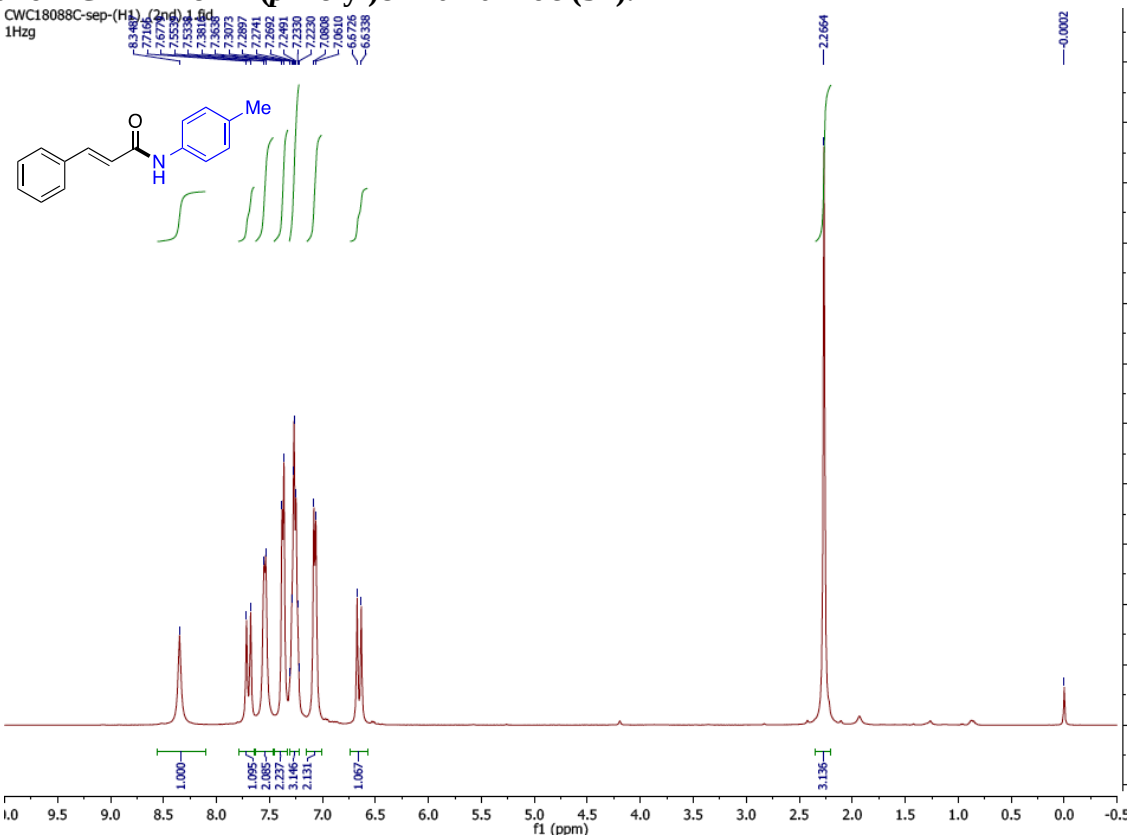


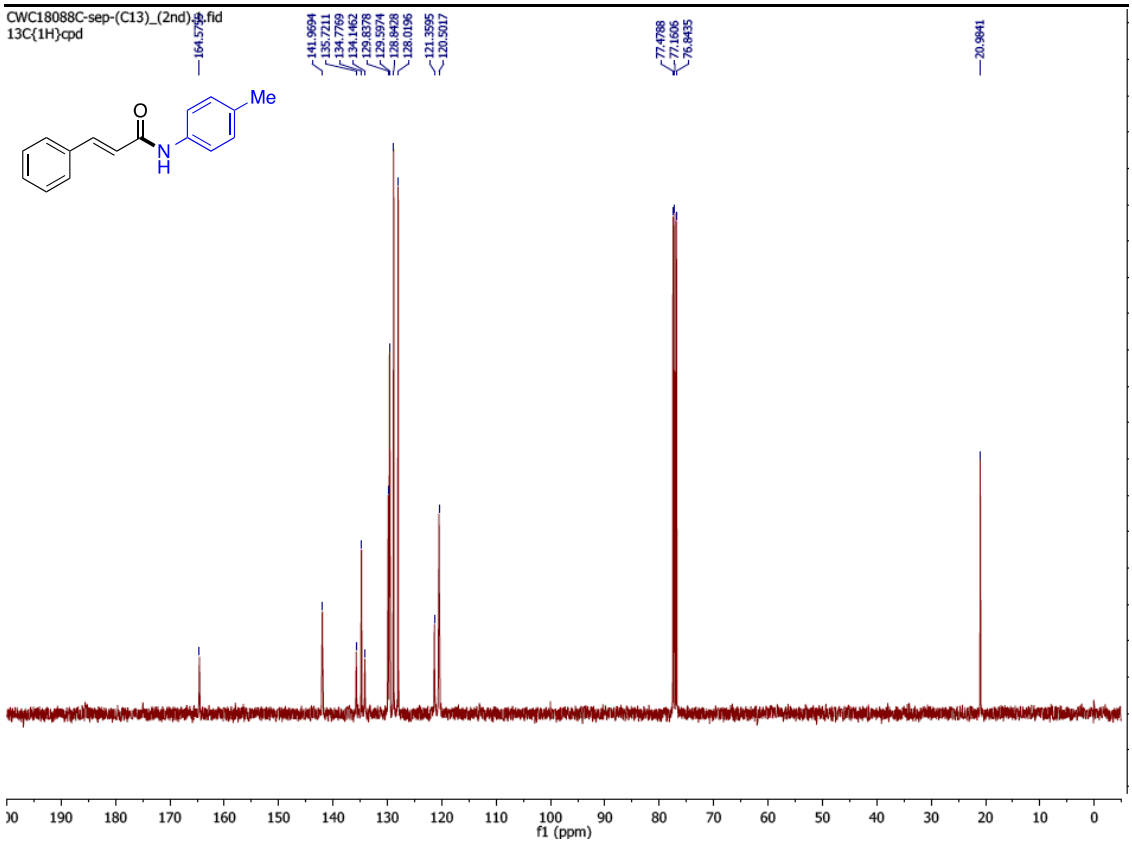


^{1}H and ^{13}C NMR of *N*-(*p*-Tolyl)undec-10-enamide (3j).

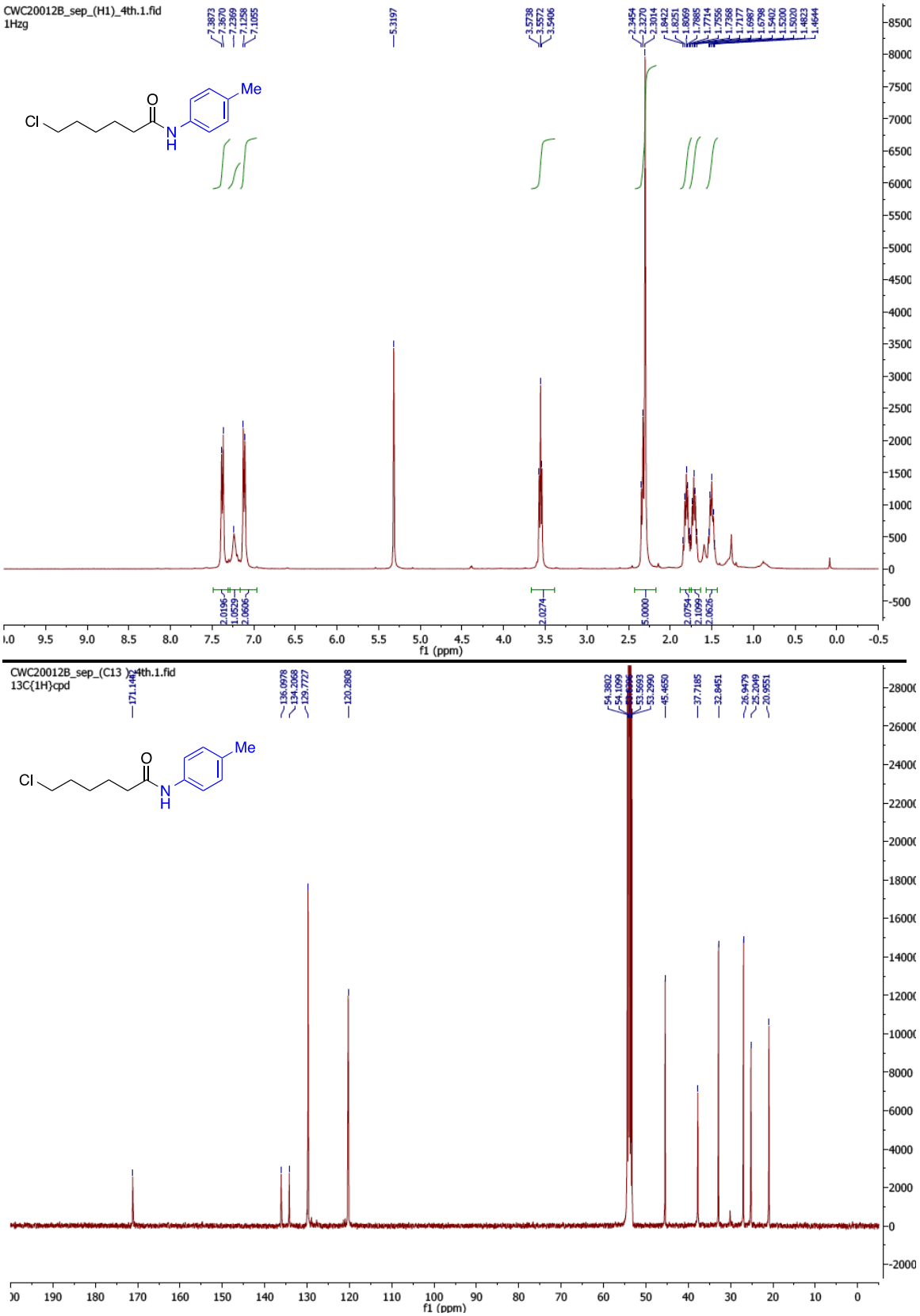


^{1}H and ^{13}C NMR of *N*-(*p*-Tolyl)cinnamamide (3k).

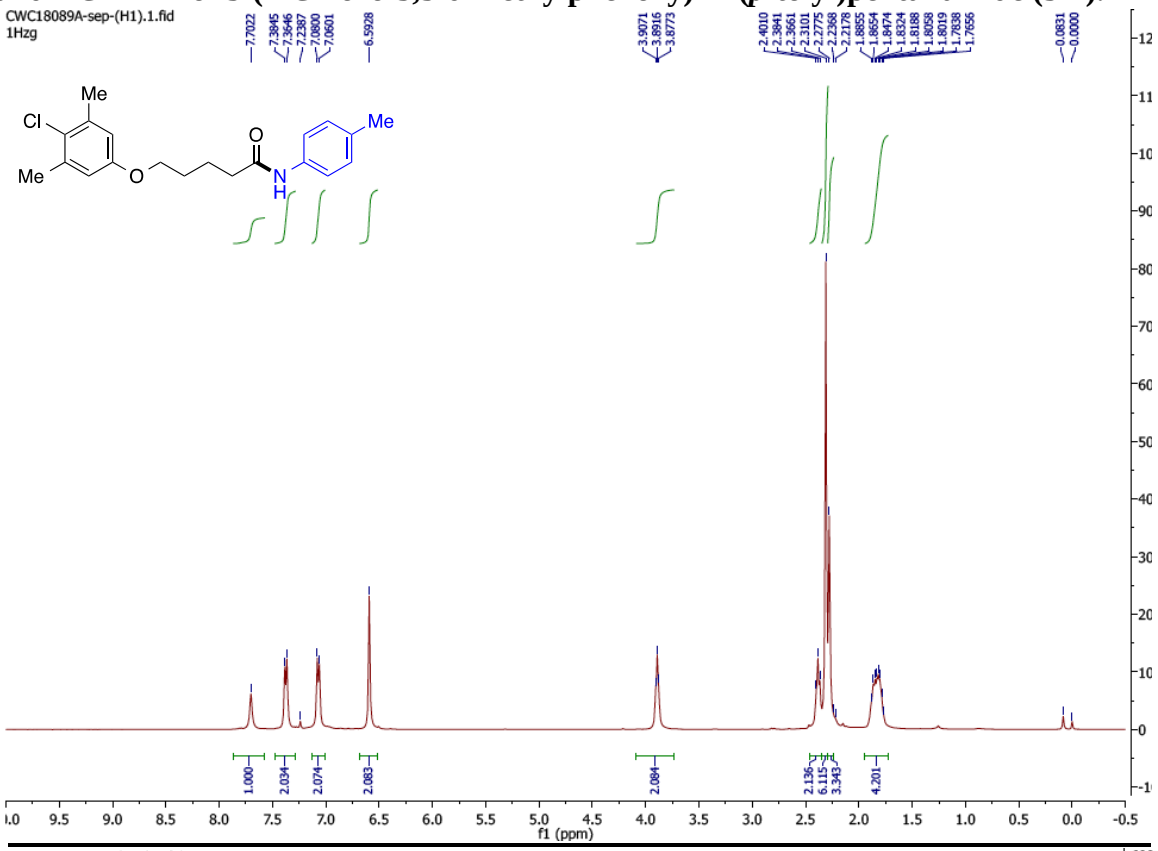


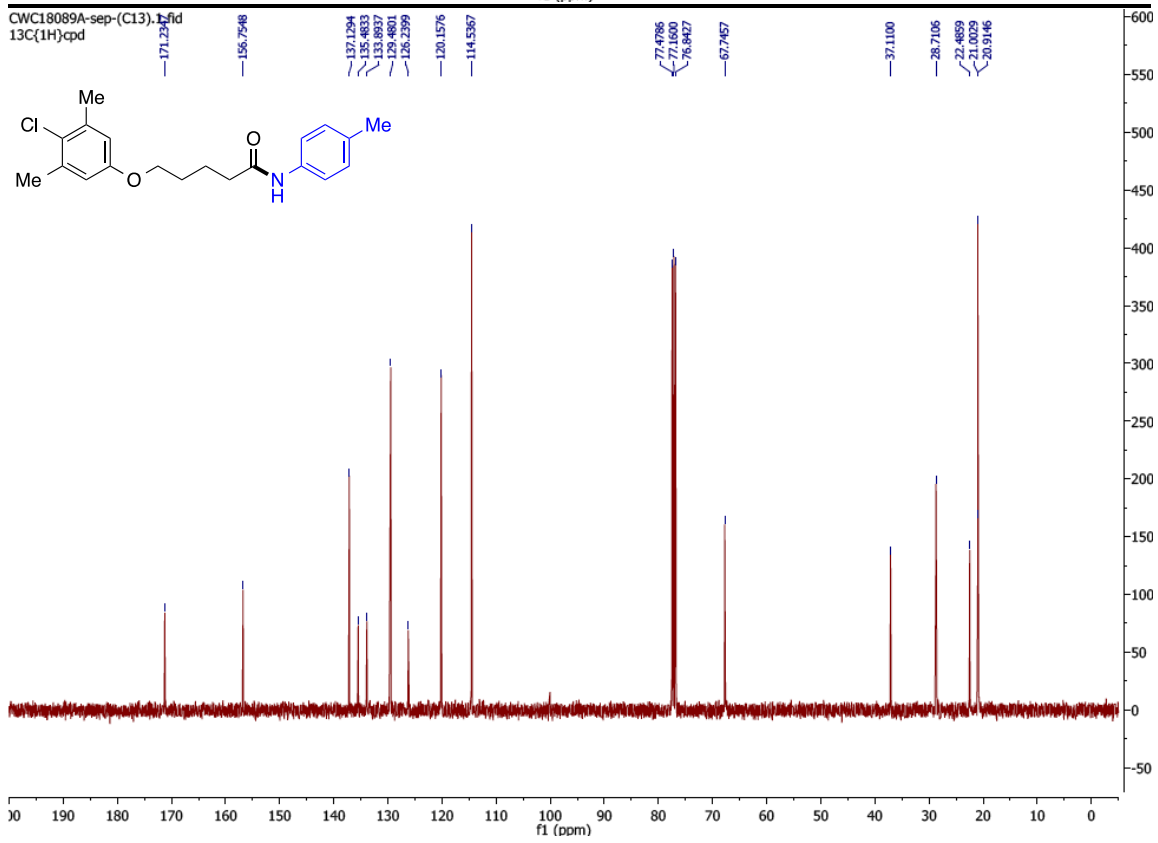


^{1}H and ^{13}C NMR of 6-Chloro-*N*-(*p*-tolyl)hexanamide (3l).

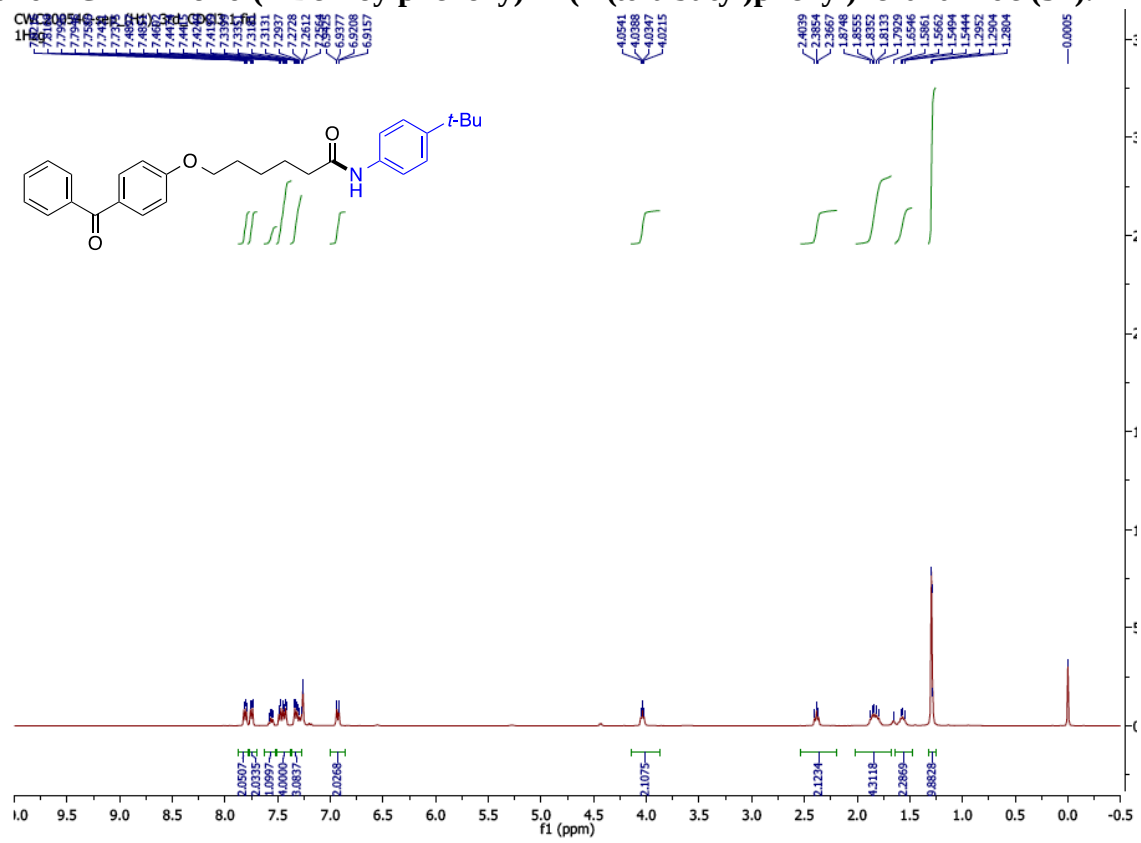


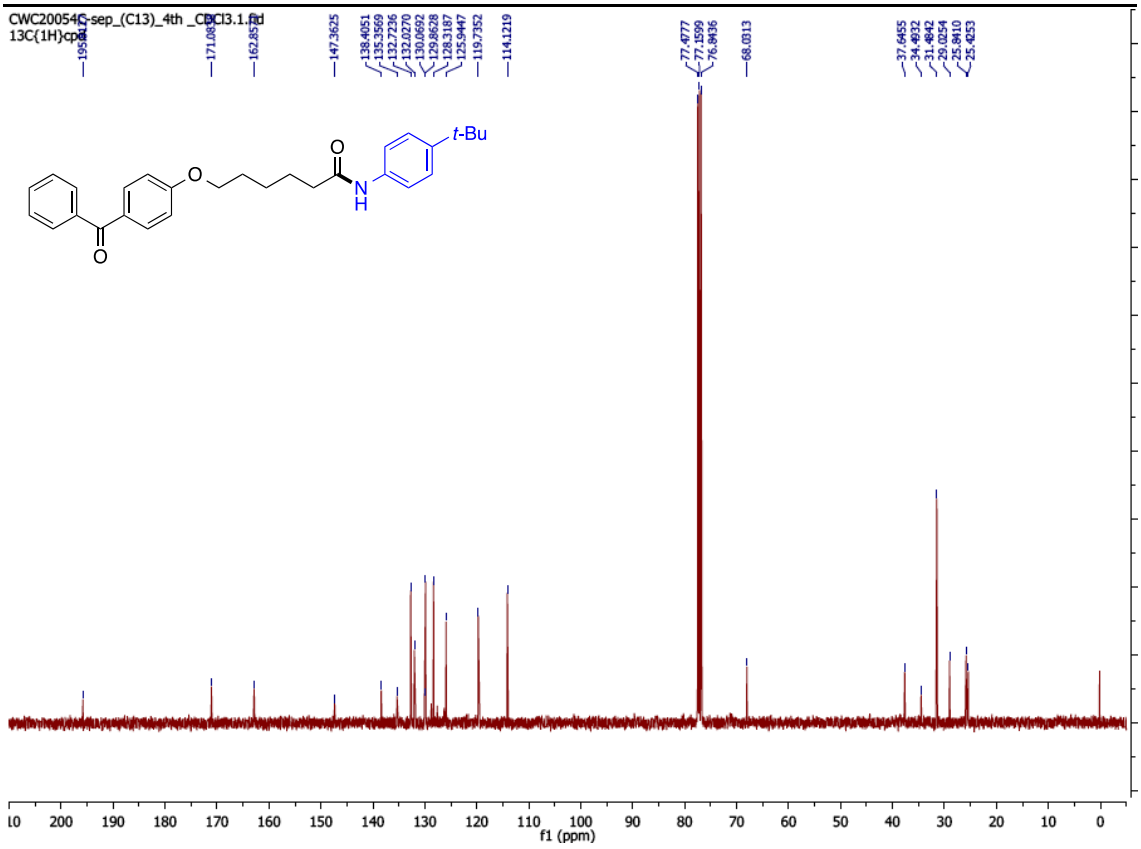
^{1}H and ^{13}C NMR of 5-(4-Chloro-3,5-dimethylphenoxy)-*N*-(*p*-tolyl)pentanamide (3m).



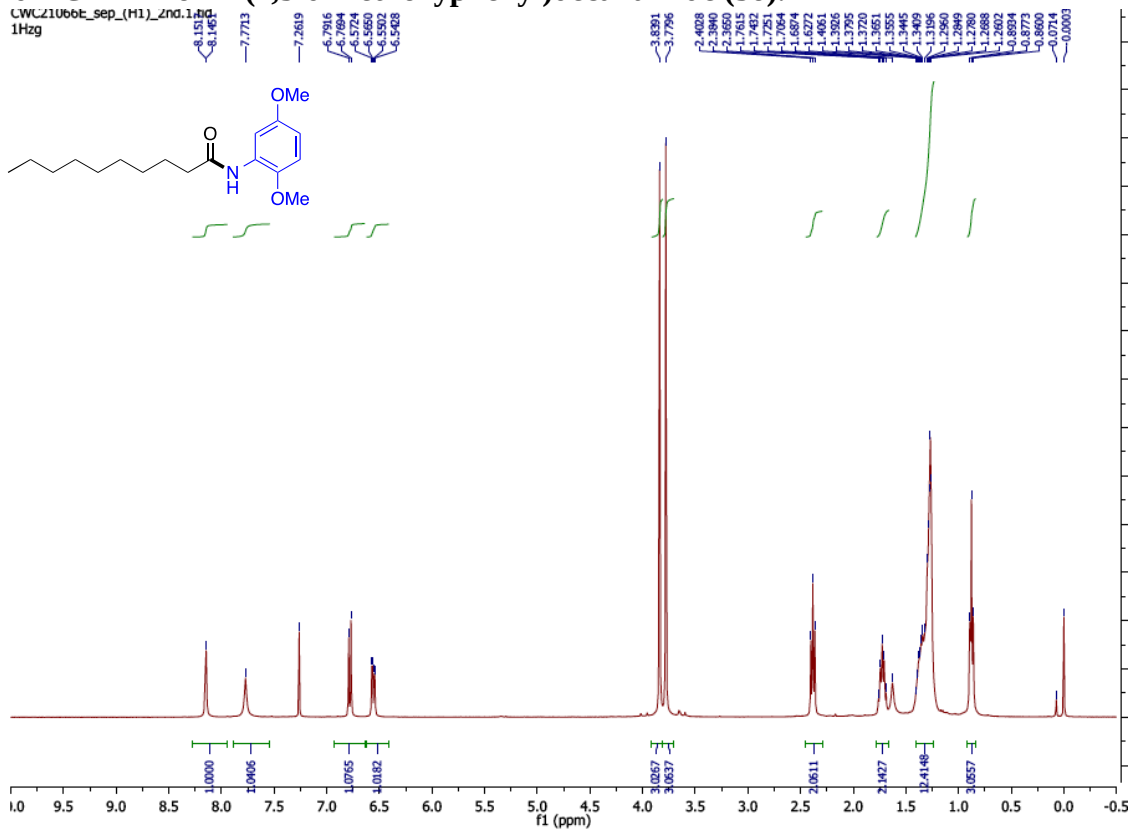


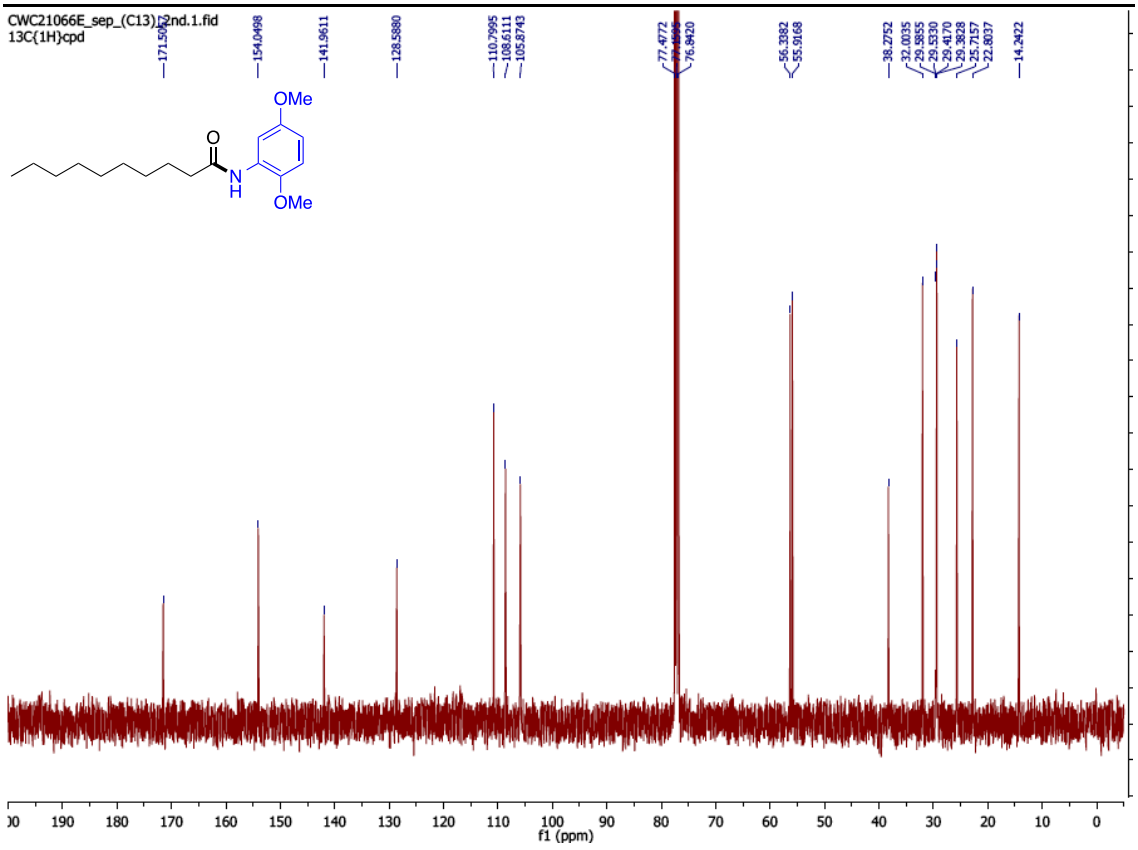
^{1}H and ^{13}C NMR of 6-(4-Benzoylphenoxy)-*N*-(4-(*tert*-butyl)phenyl)hexanamide (3n).



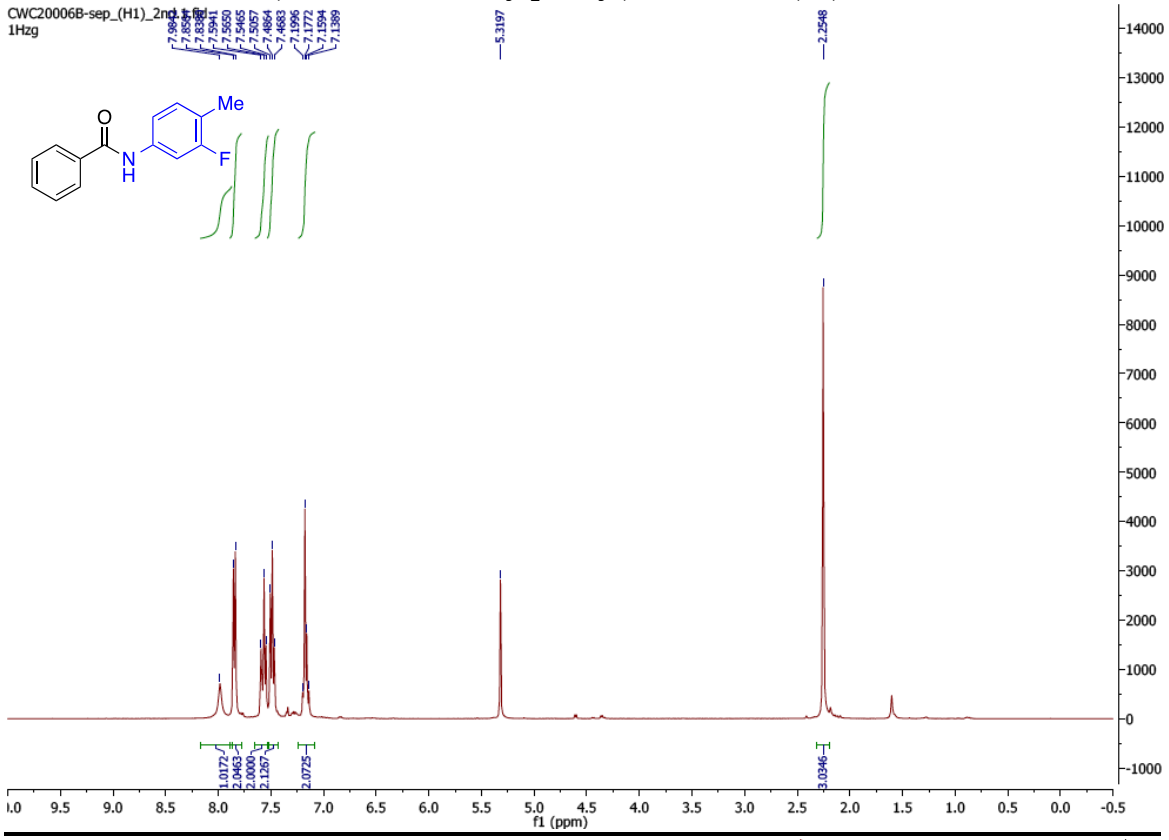


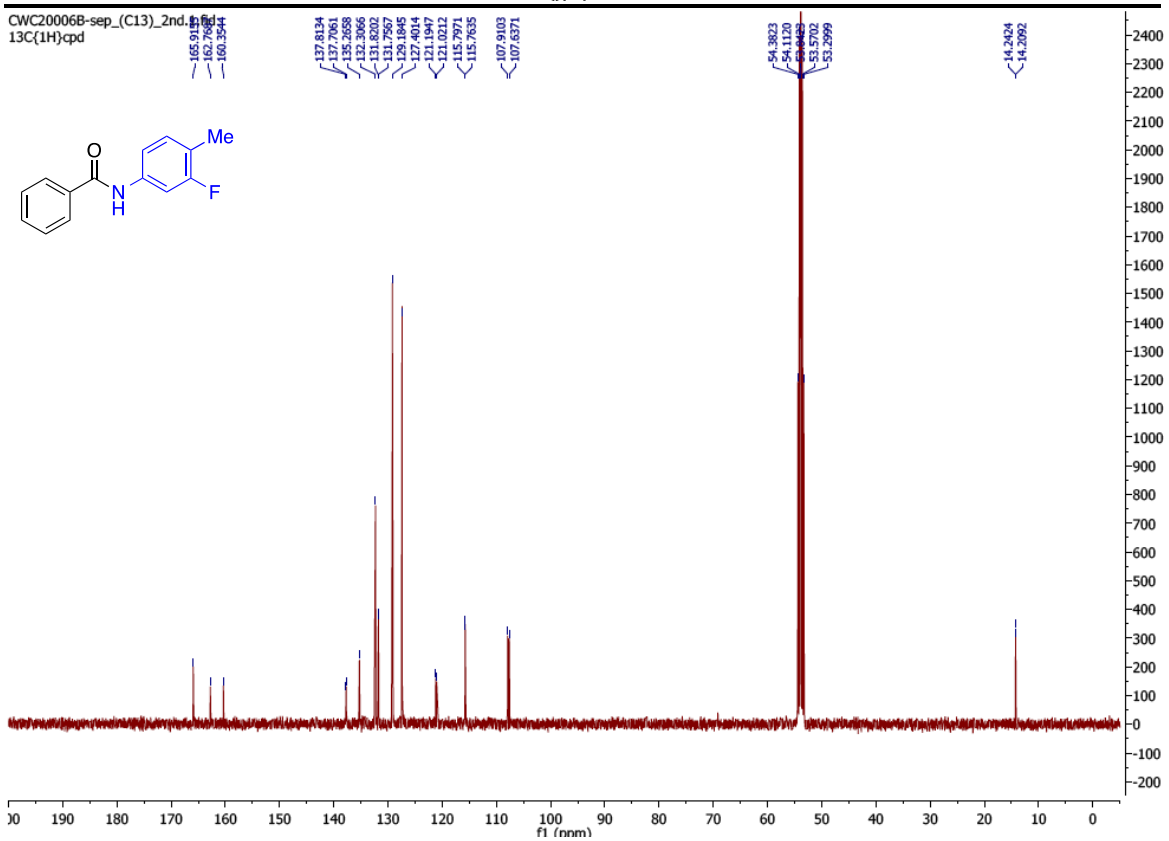
^{1}H and ^{13}C NMR of *N*-(2,5-dimethoxyphenyl)decanamide (3o).



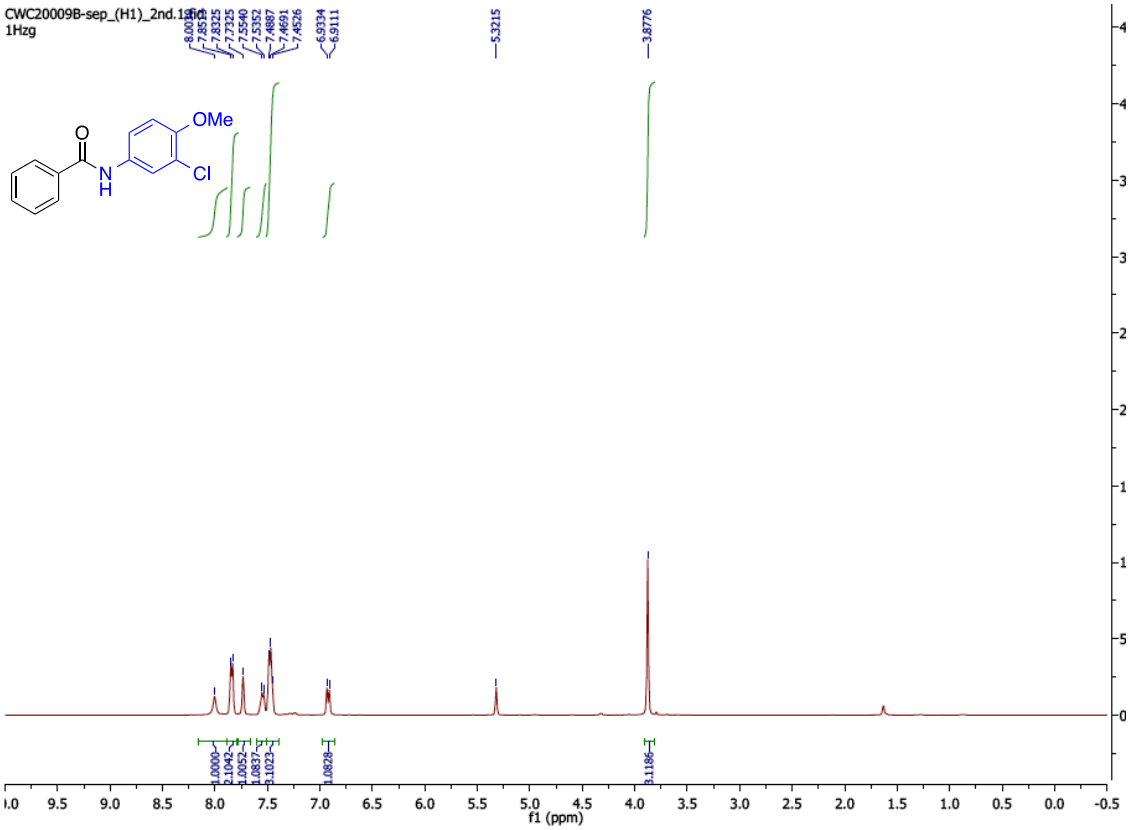


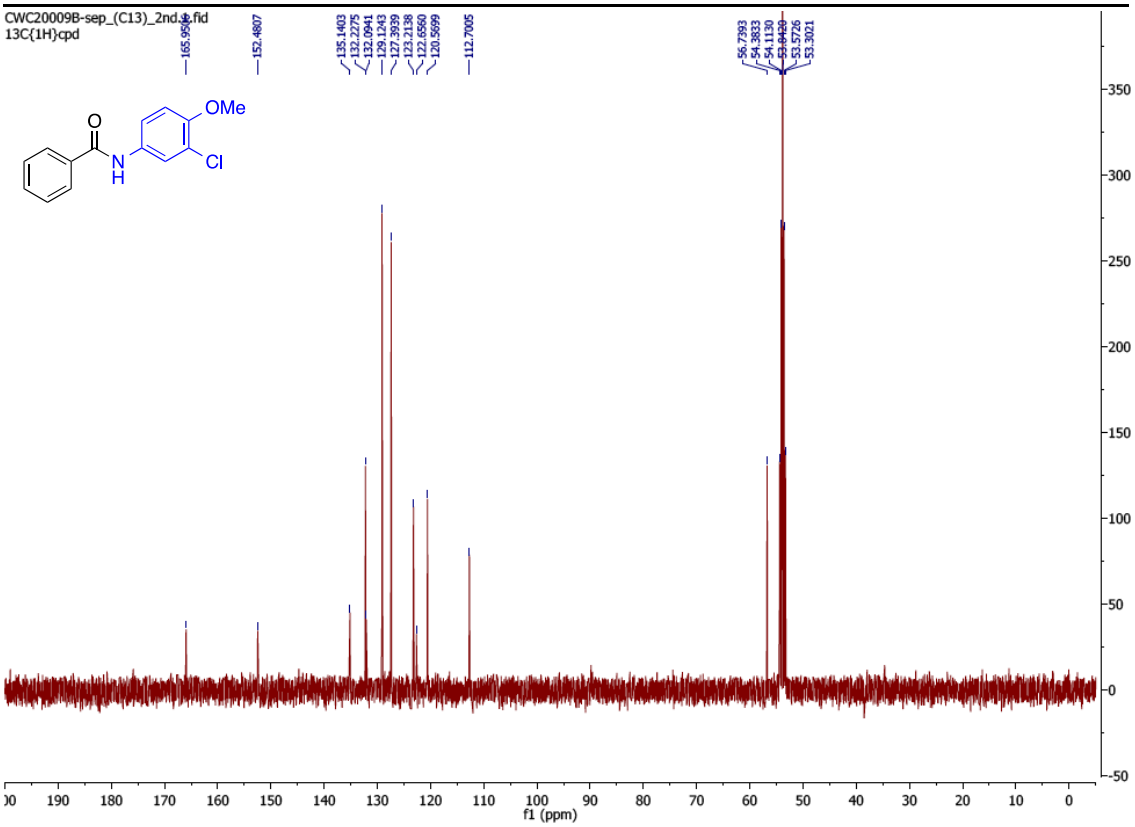
^{1}H and ^{13}C NMR of *N*-(3-Fluoro-4-methylphenyl)benzamide (4a).



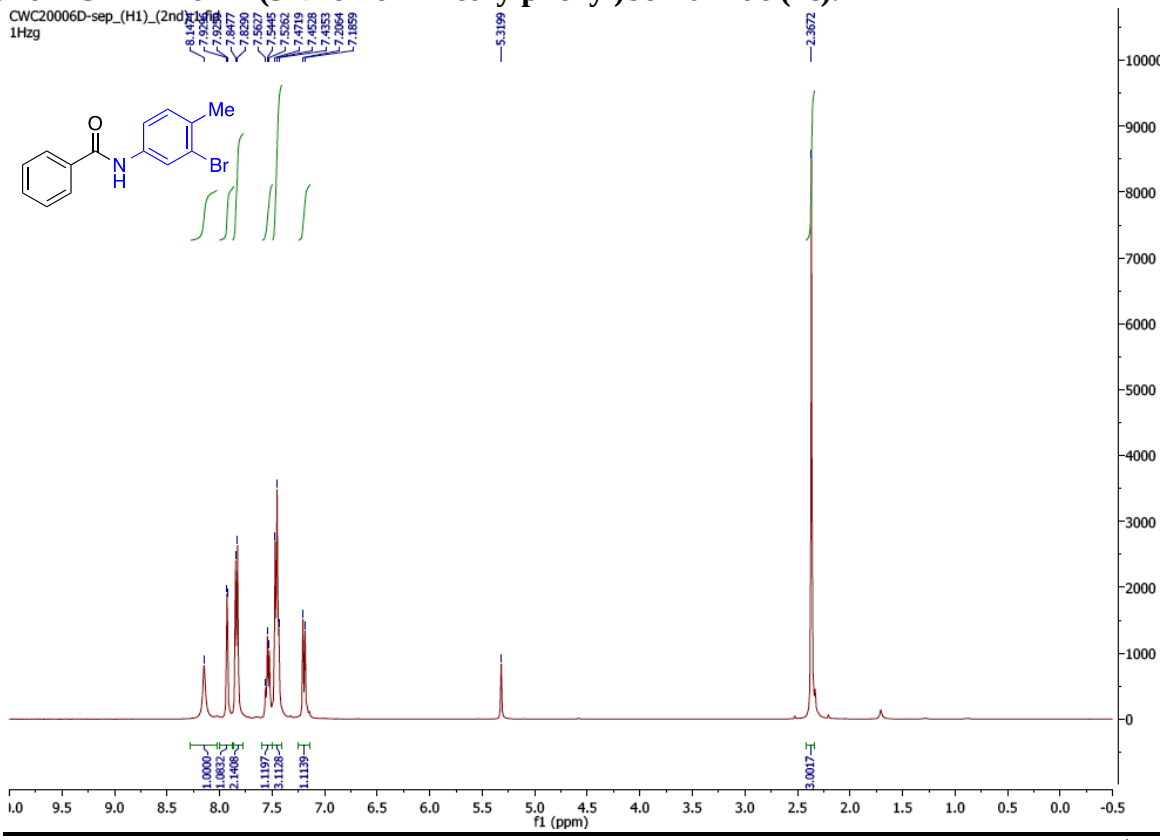


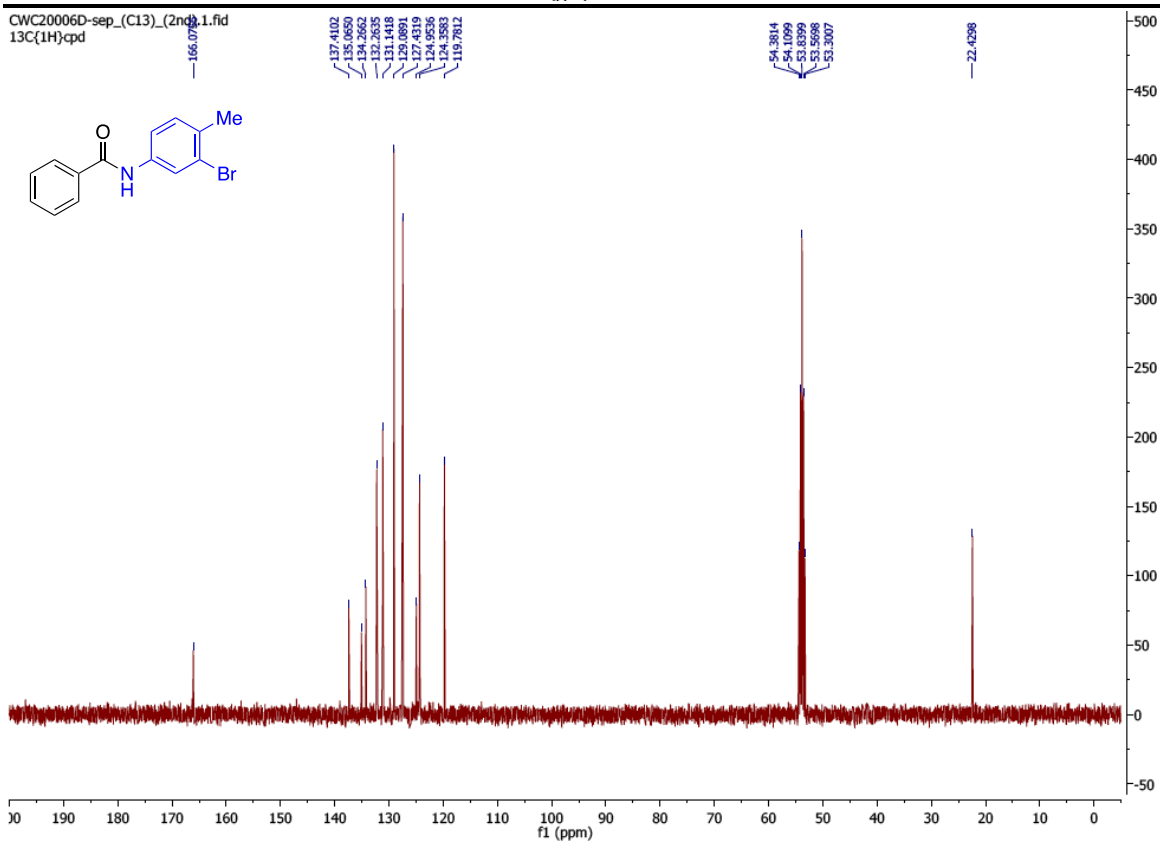
^{1}H and ^{13}C NMR of *N*-(3-Chloro-4-methoxyphenyl)benzamide (4b).



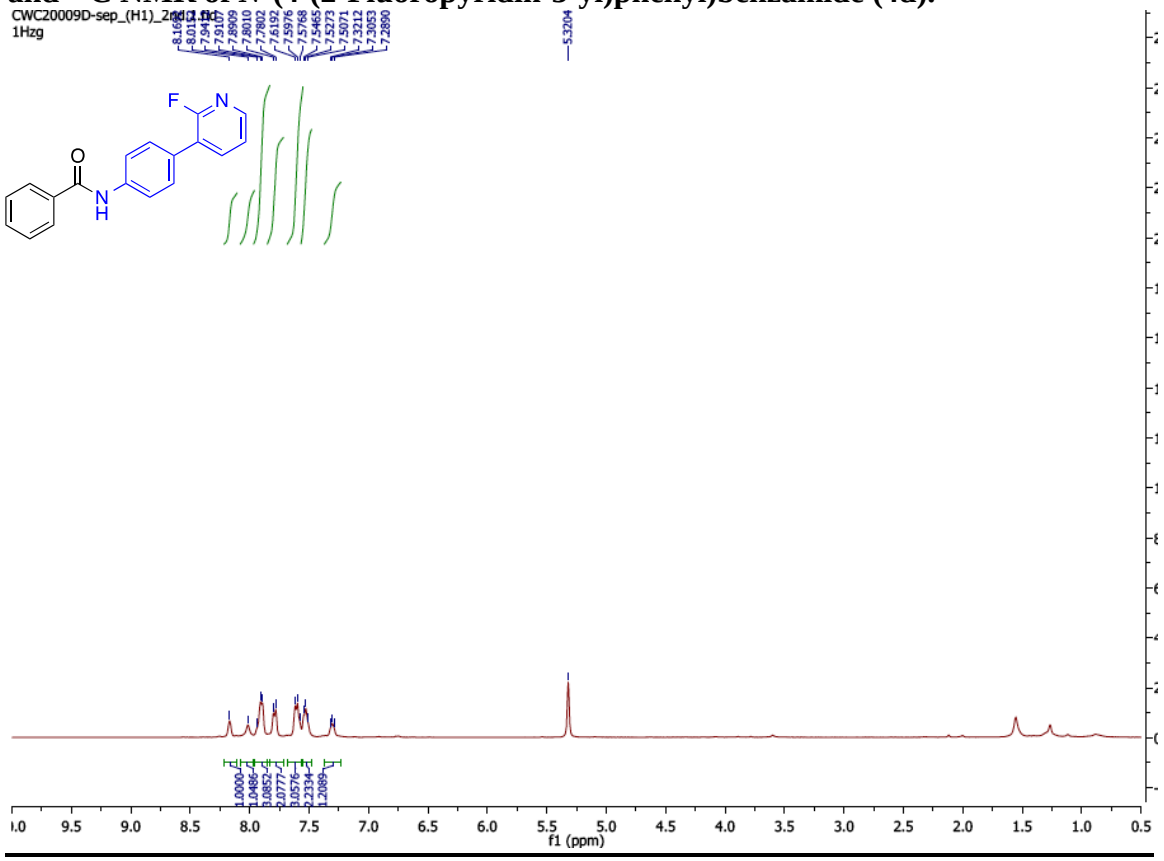


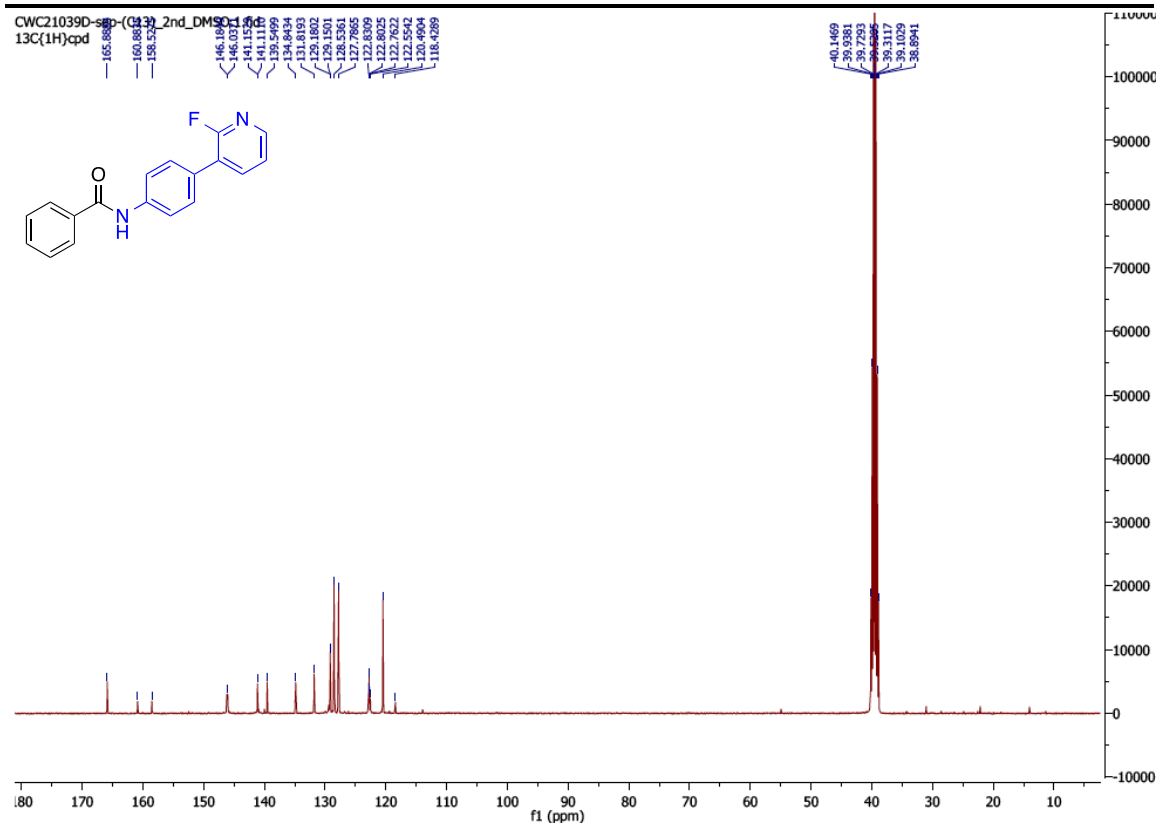
^{1}H and ^{13}C NMR of *N*-(3-Bromo-4-methylphenyl)benzamide (4c).



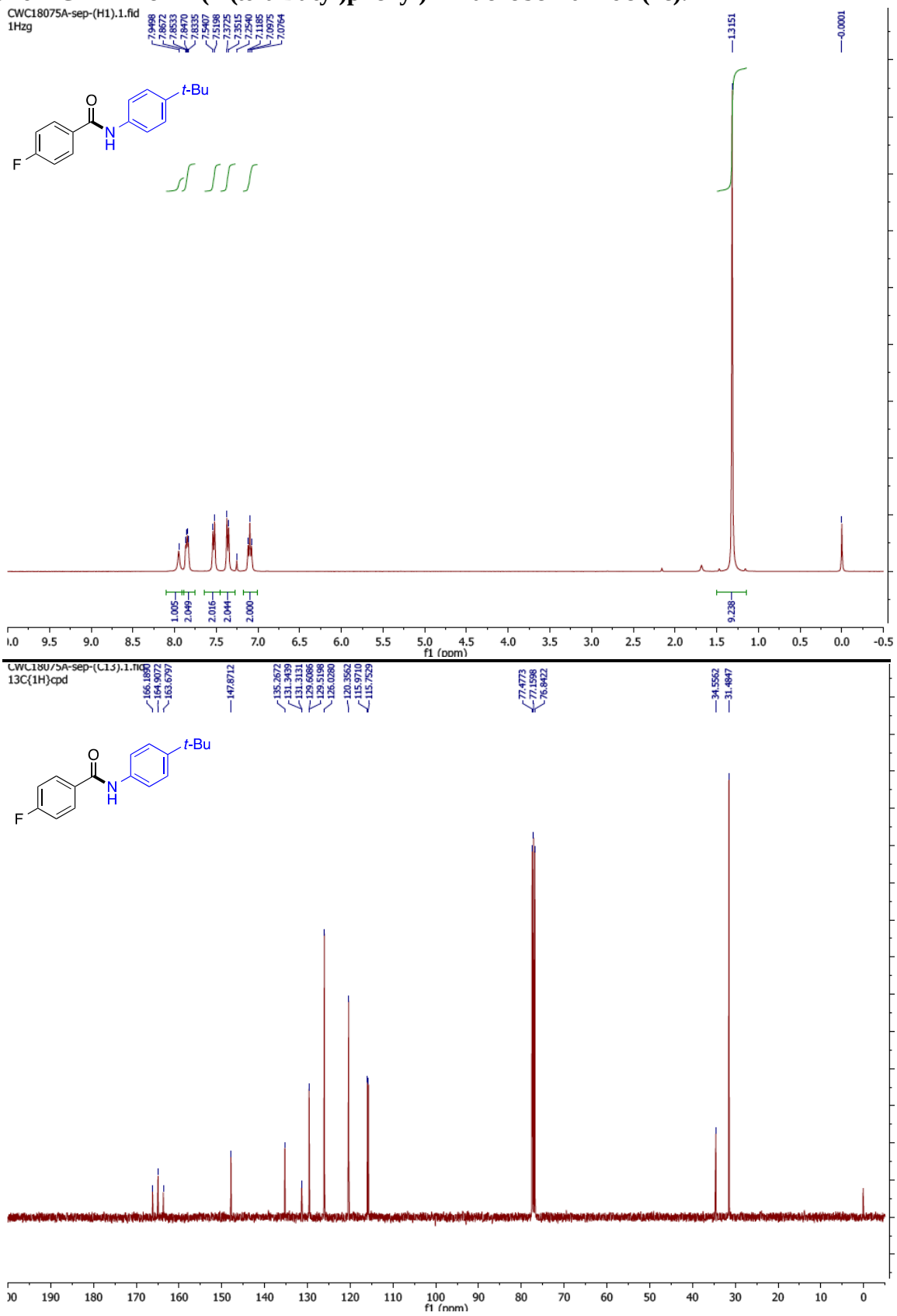


^{1}H and ^{13}C NMR of *N*-(4-(2-Fluoropyridin-3-yl)phenyl)benzamide (4d).

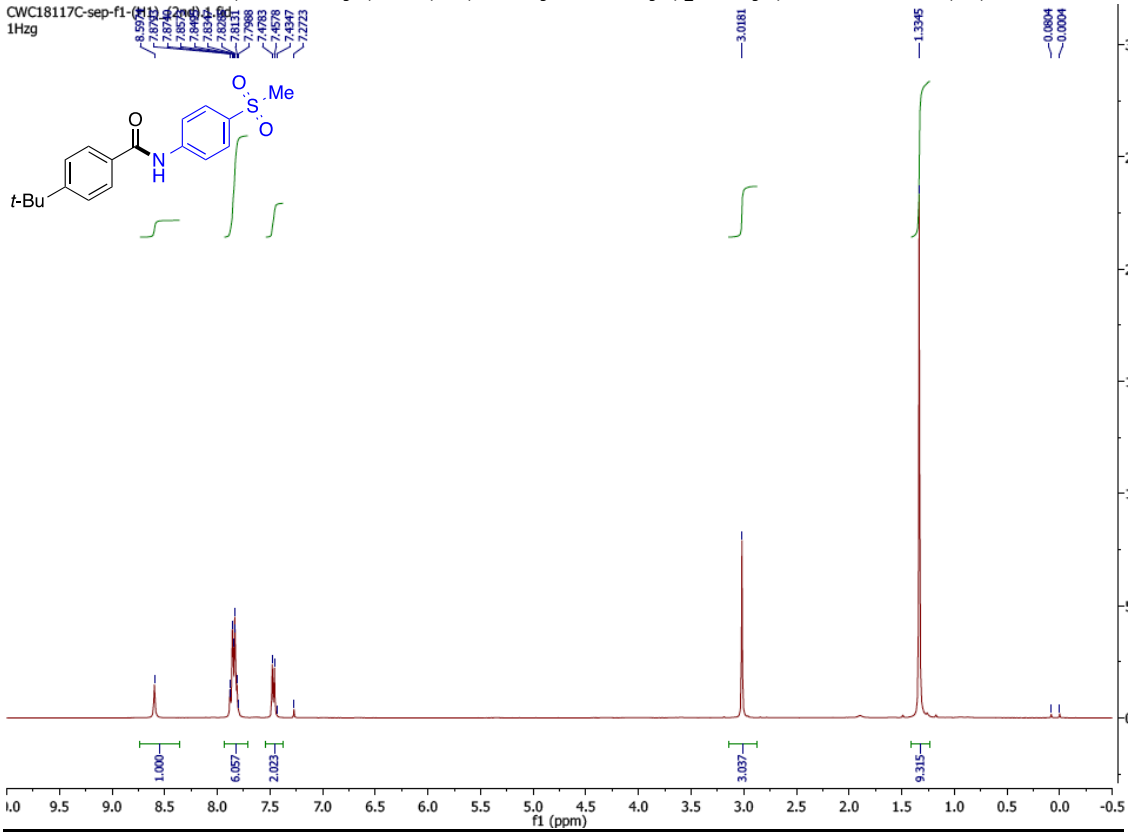


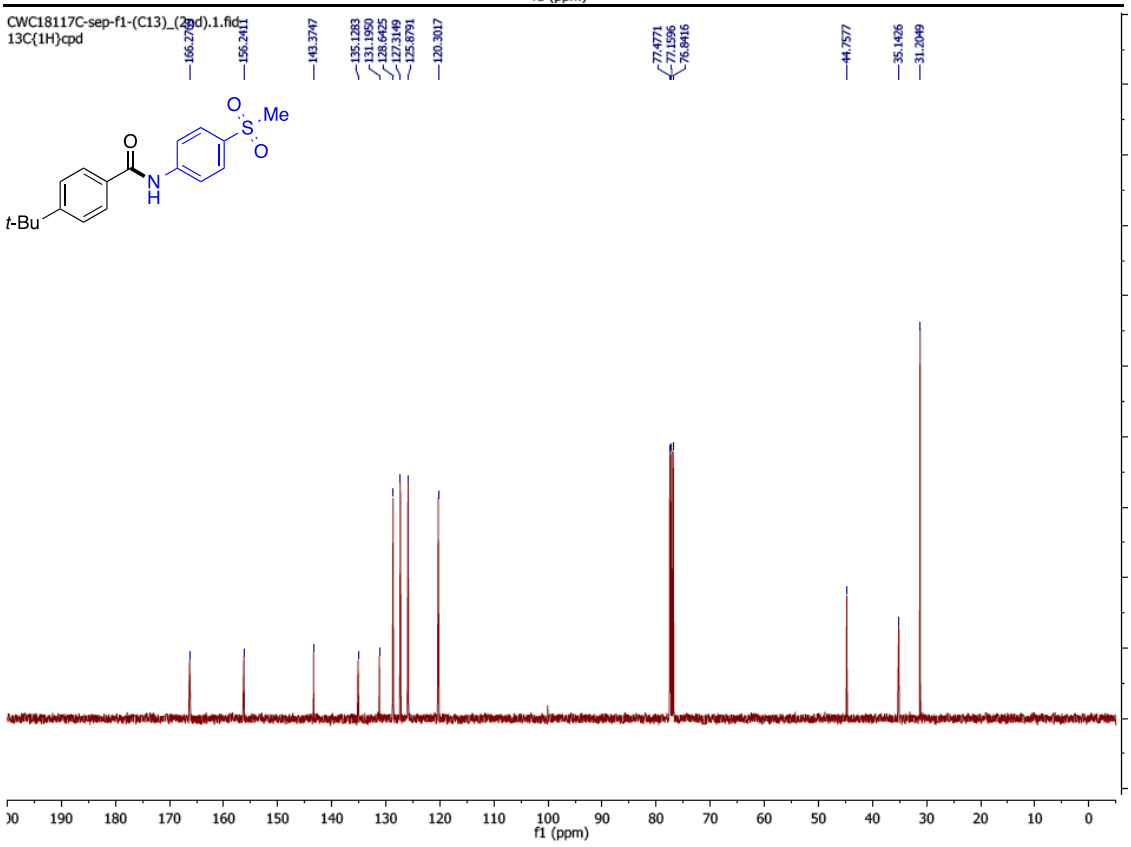


^{1}H and ^{13}C NMR of *N*-(4-(*tert*-Butyl)phenyl)-4-fluorobenzamide (4e).

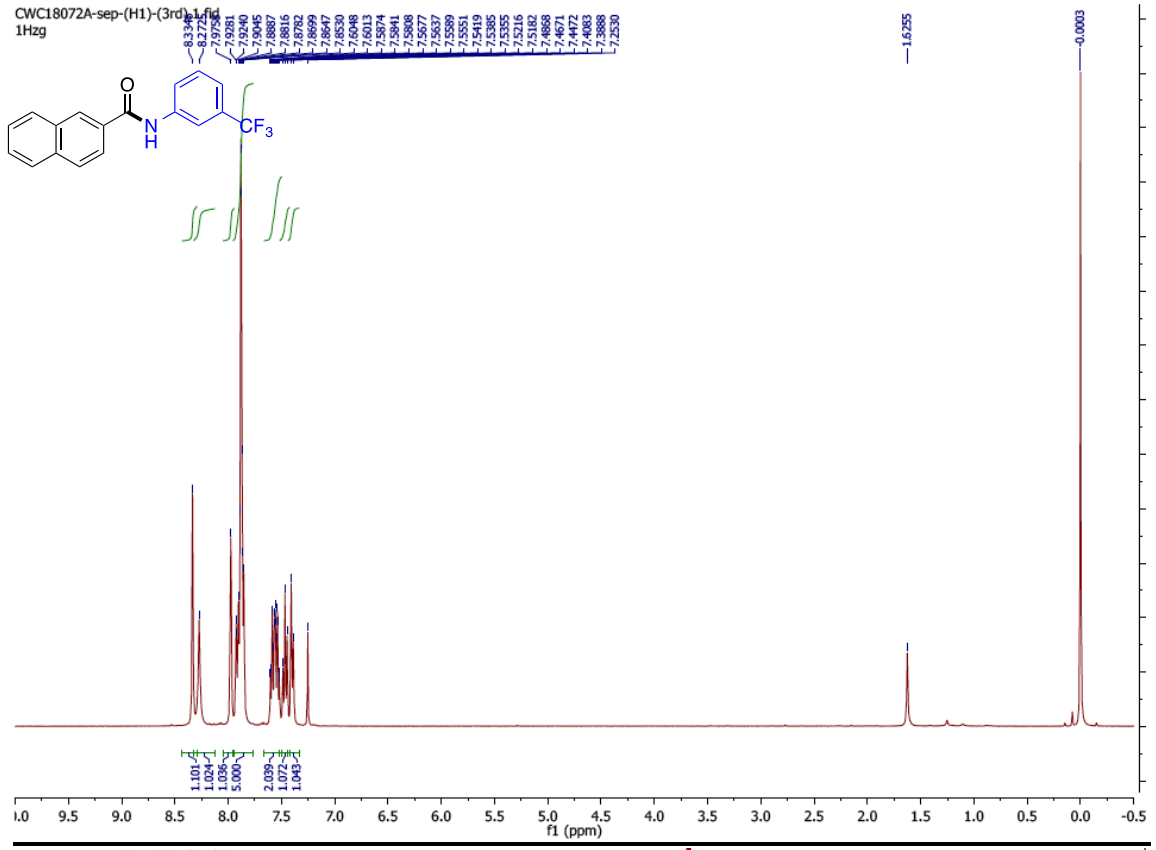


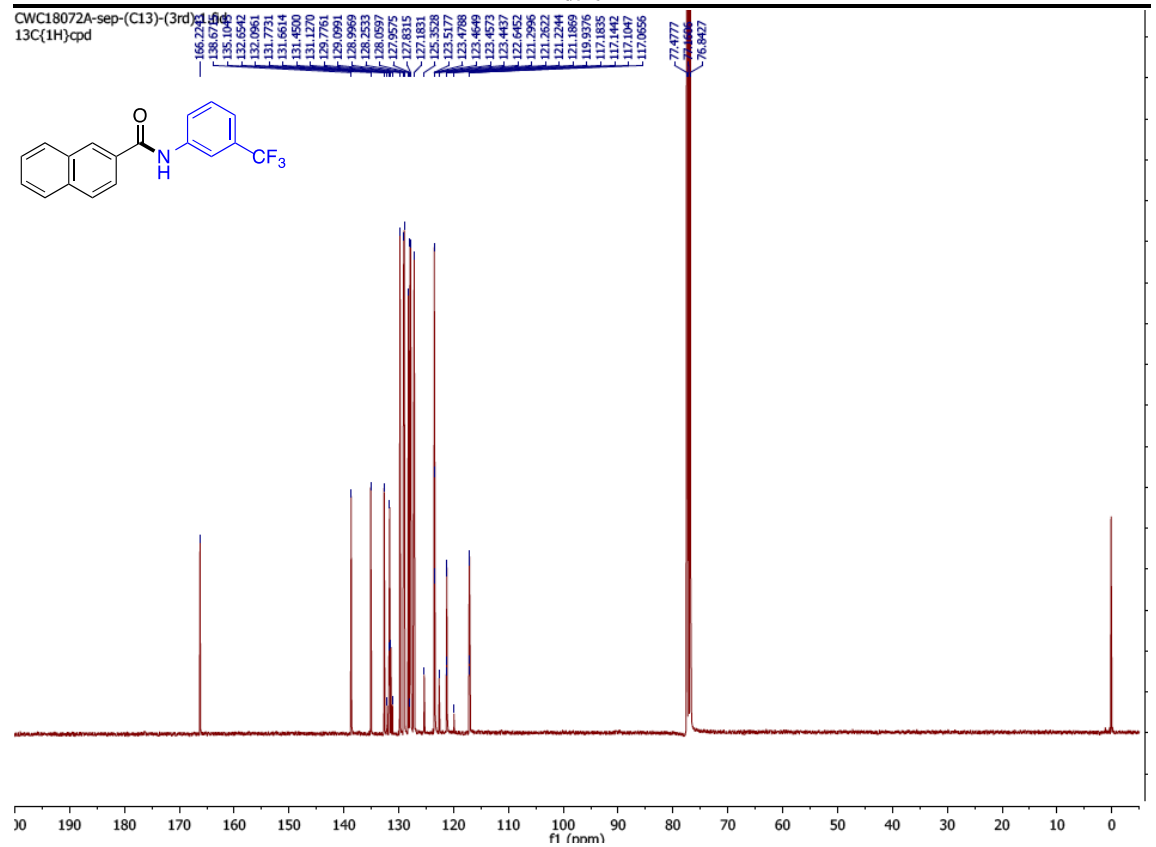
^{1}H and ^{13}C NMR of 4-(*tert*-Butyl)-*N*-(4-(methylsulfonyl)phenyl)benzamide (4f).



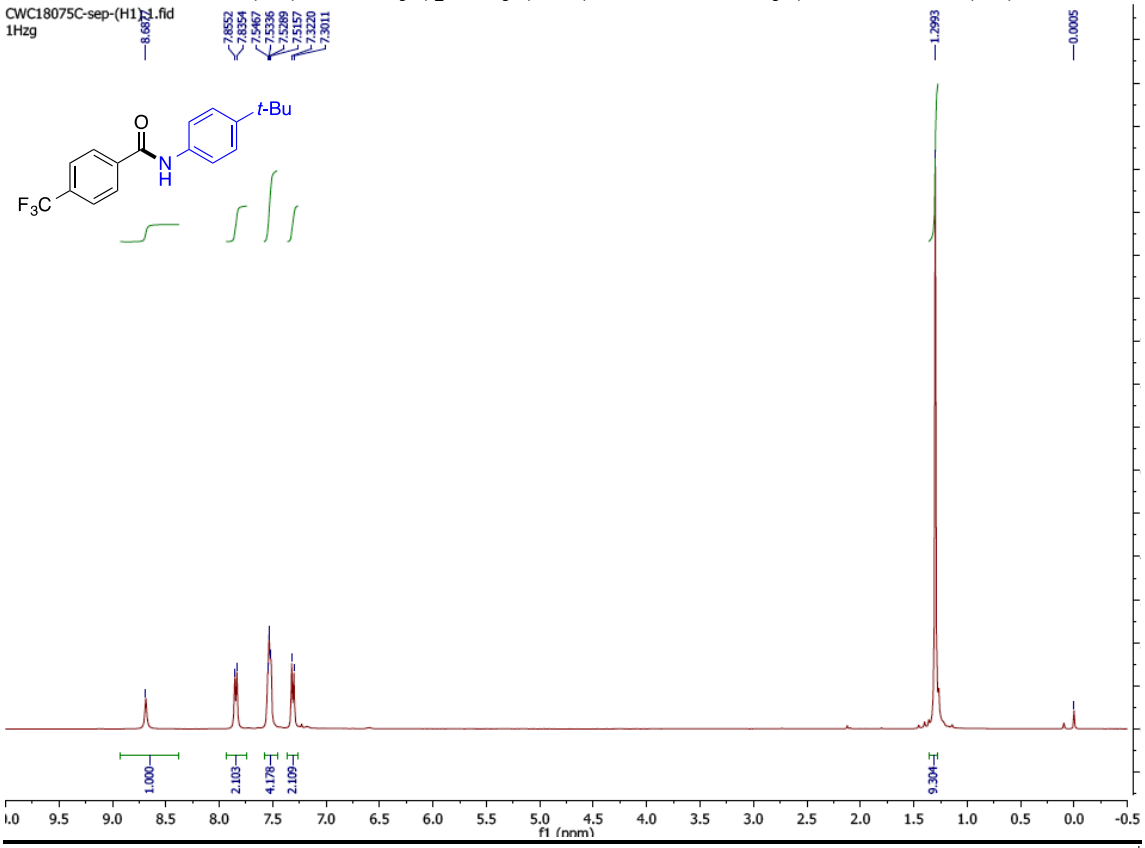


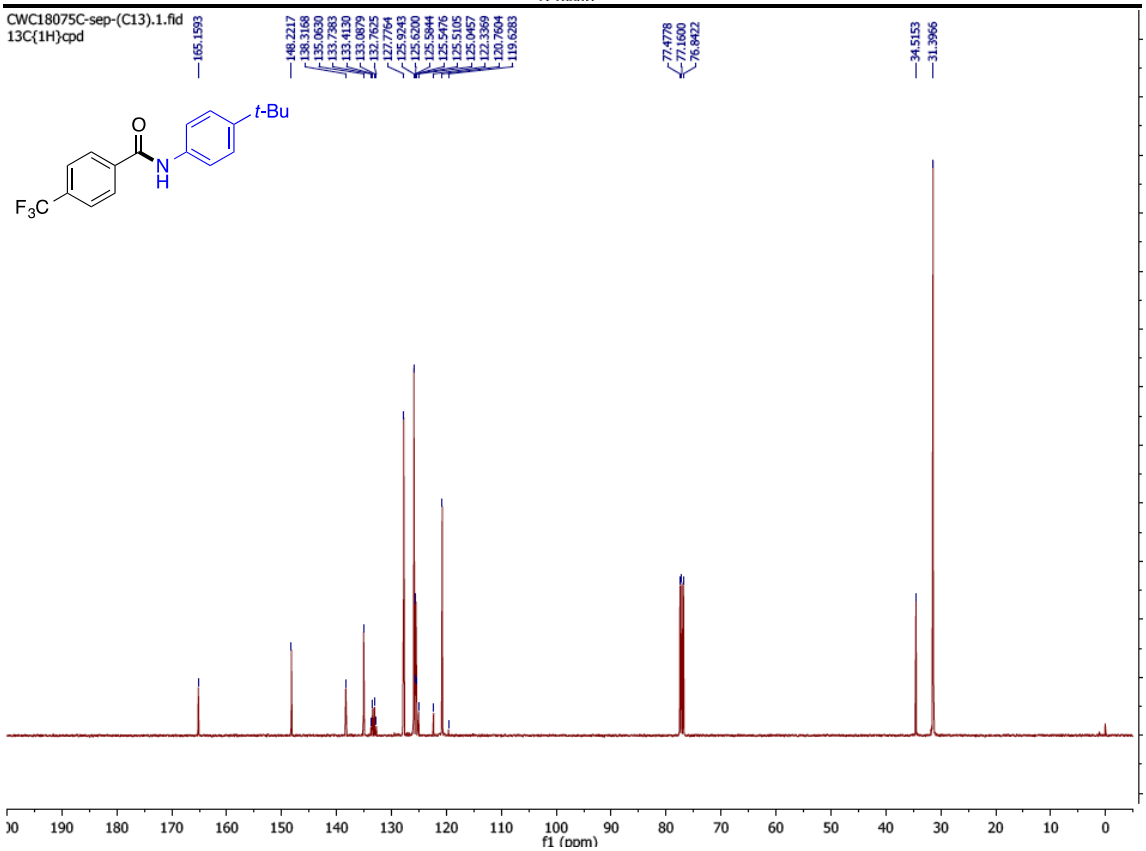
^{1}H and ^{13}C NMR of *N*-(3-(Trifluoromethyl)phenyl)-2-naphthamide (4g).



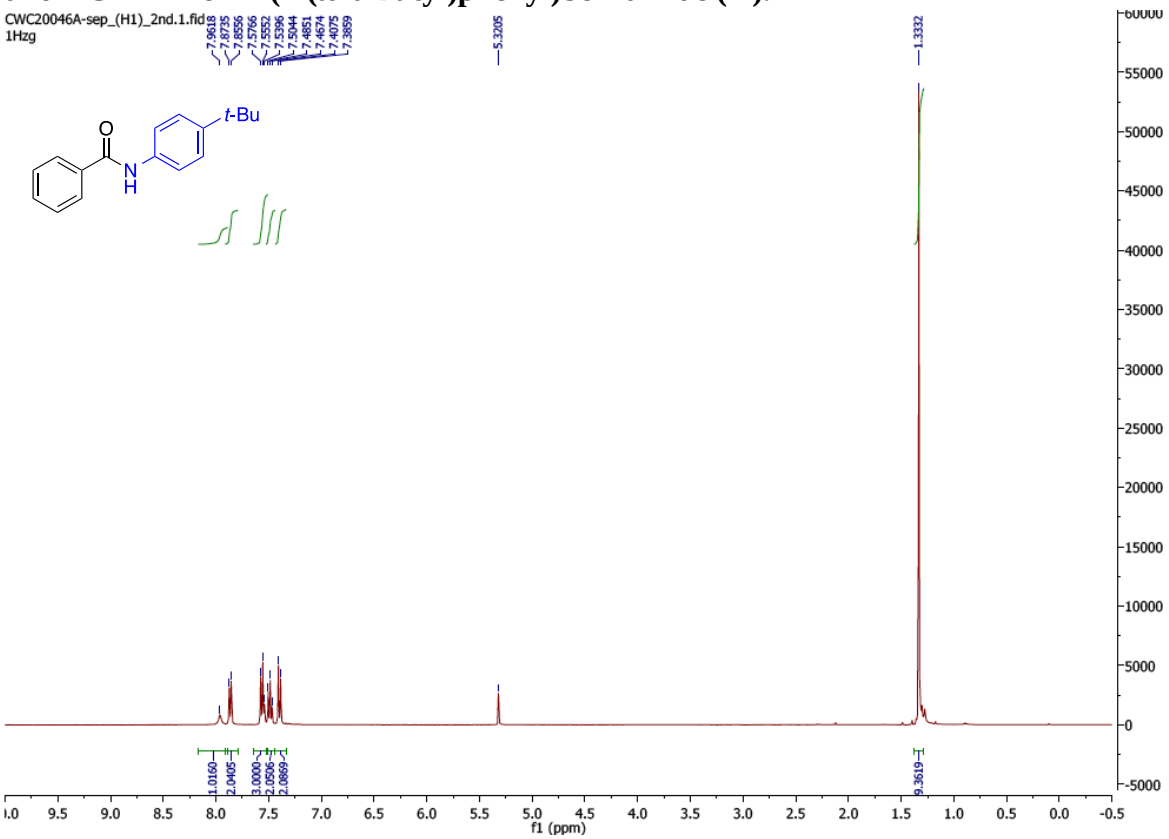


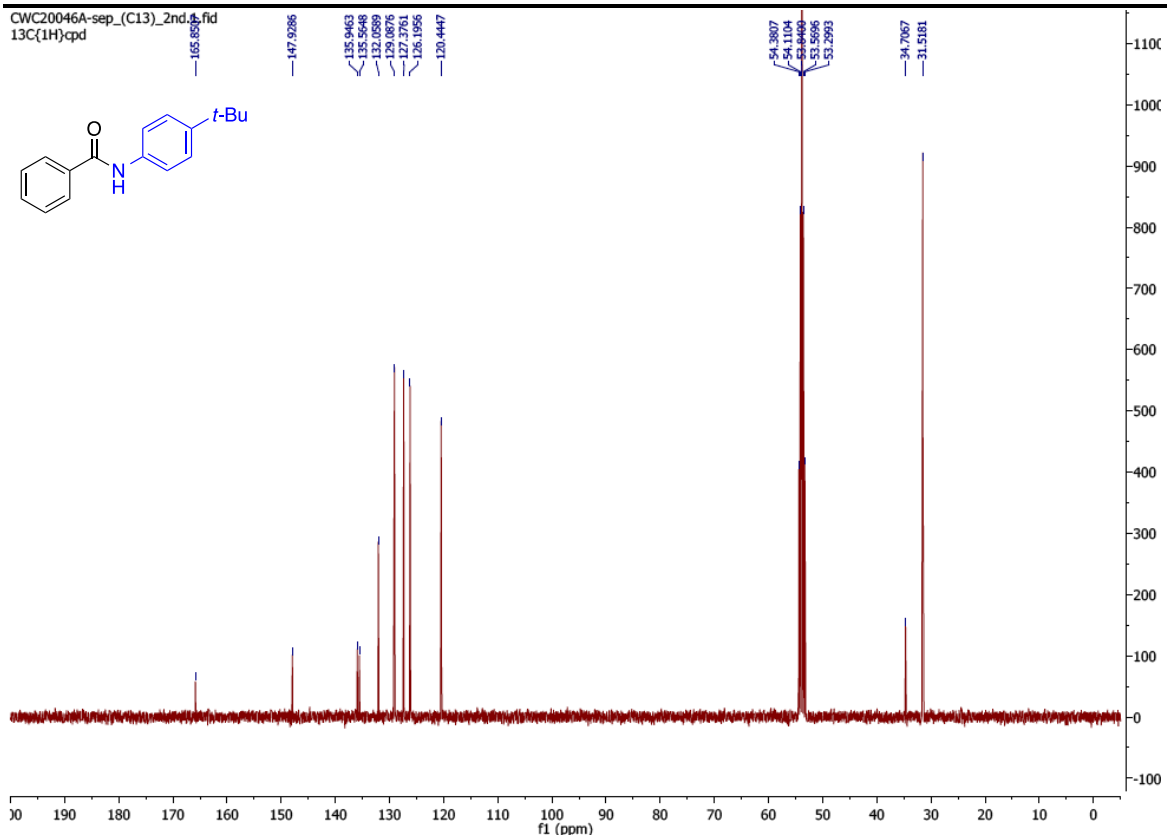
^{1}H and ^{13}C NMR of *N*-(4-(*tert*-Butyl)phenyl)-4-(trifluoromethyl)benzamide (4h).



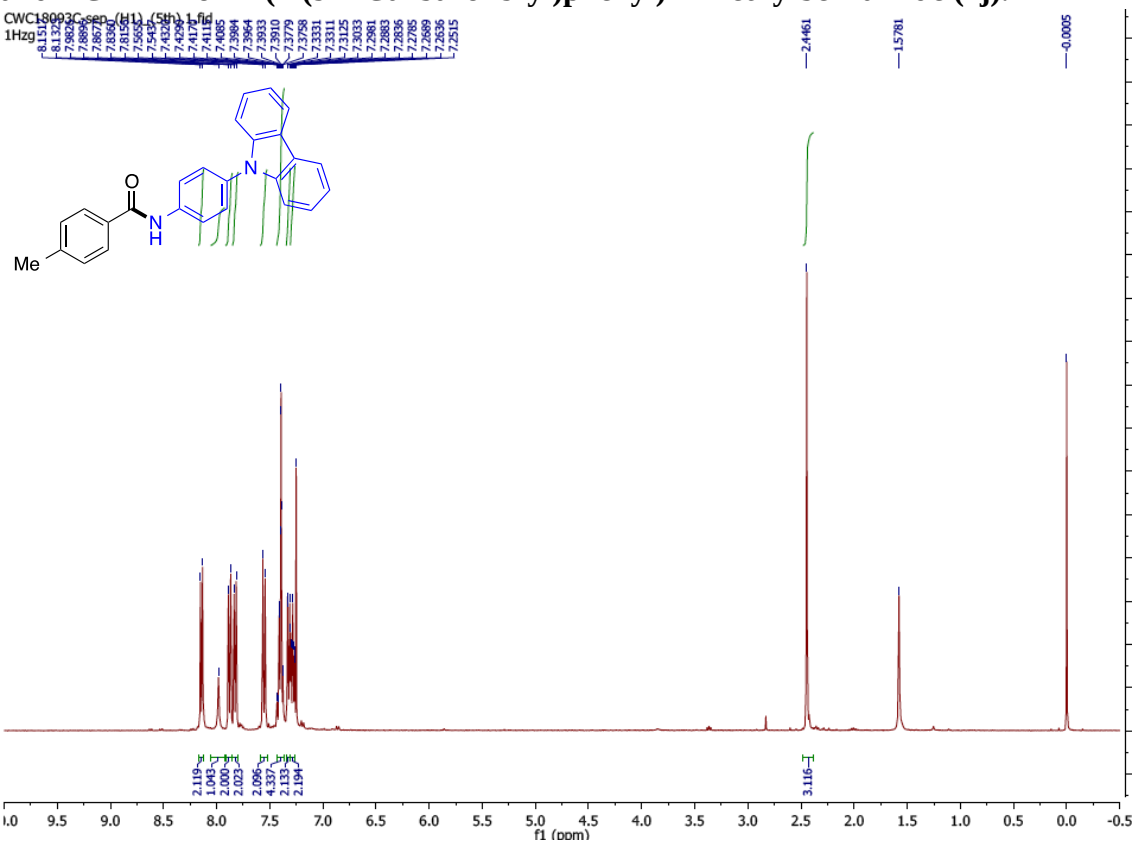


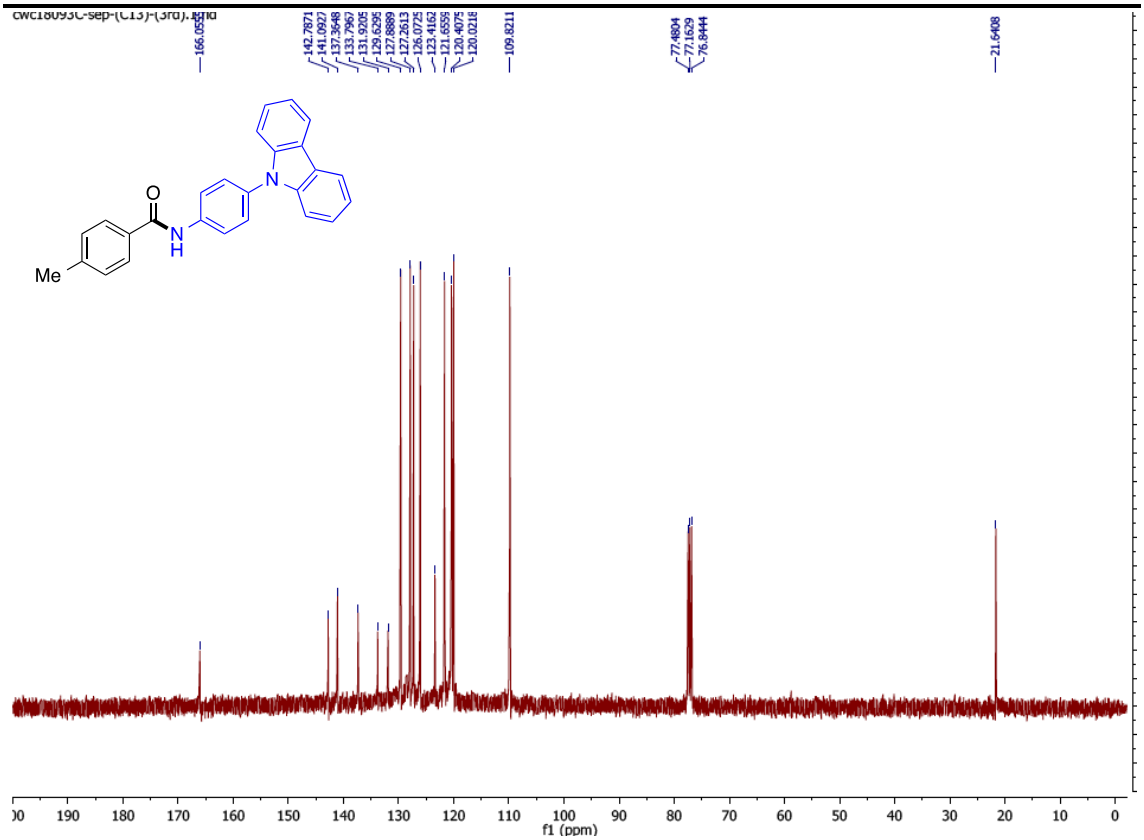
^{1}H and ^{13}C NMR of *N*-(4-(*tert*-Butyl)phenyl)benzamide (4i).



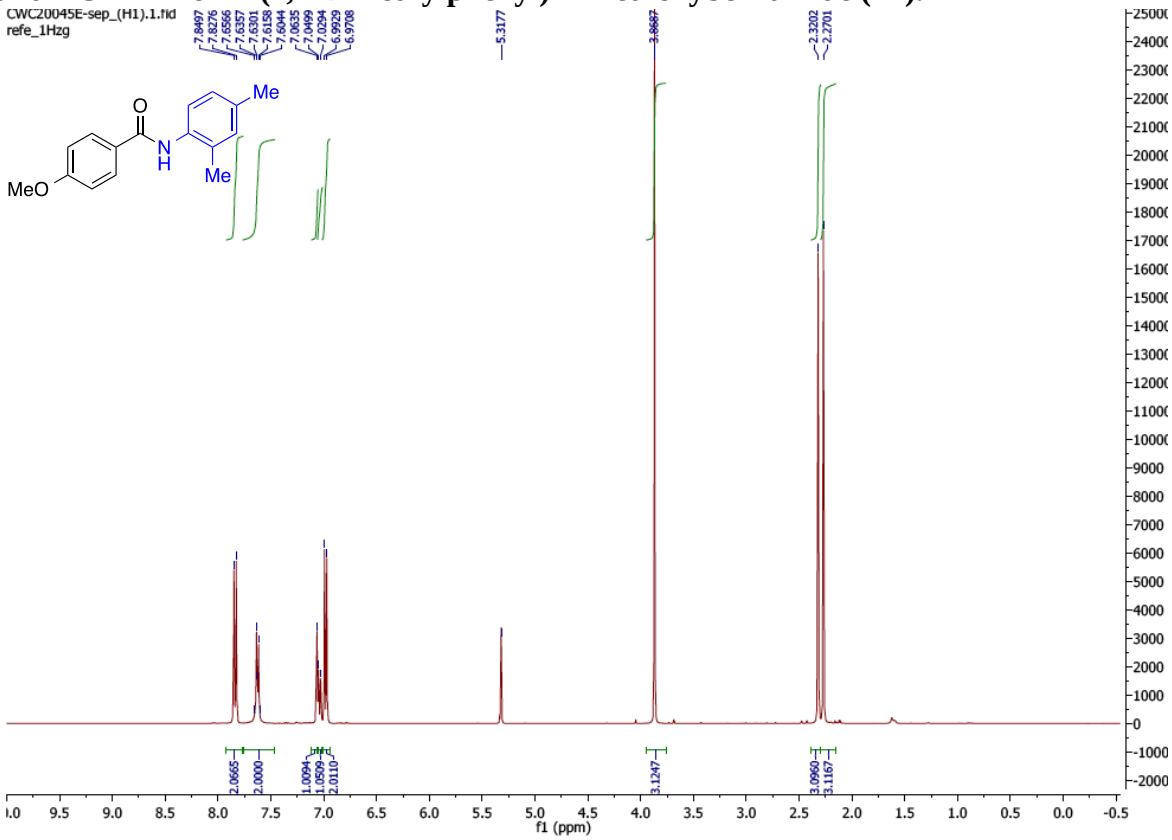


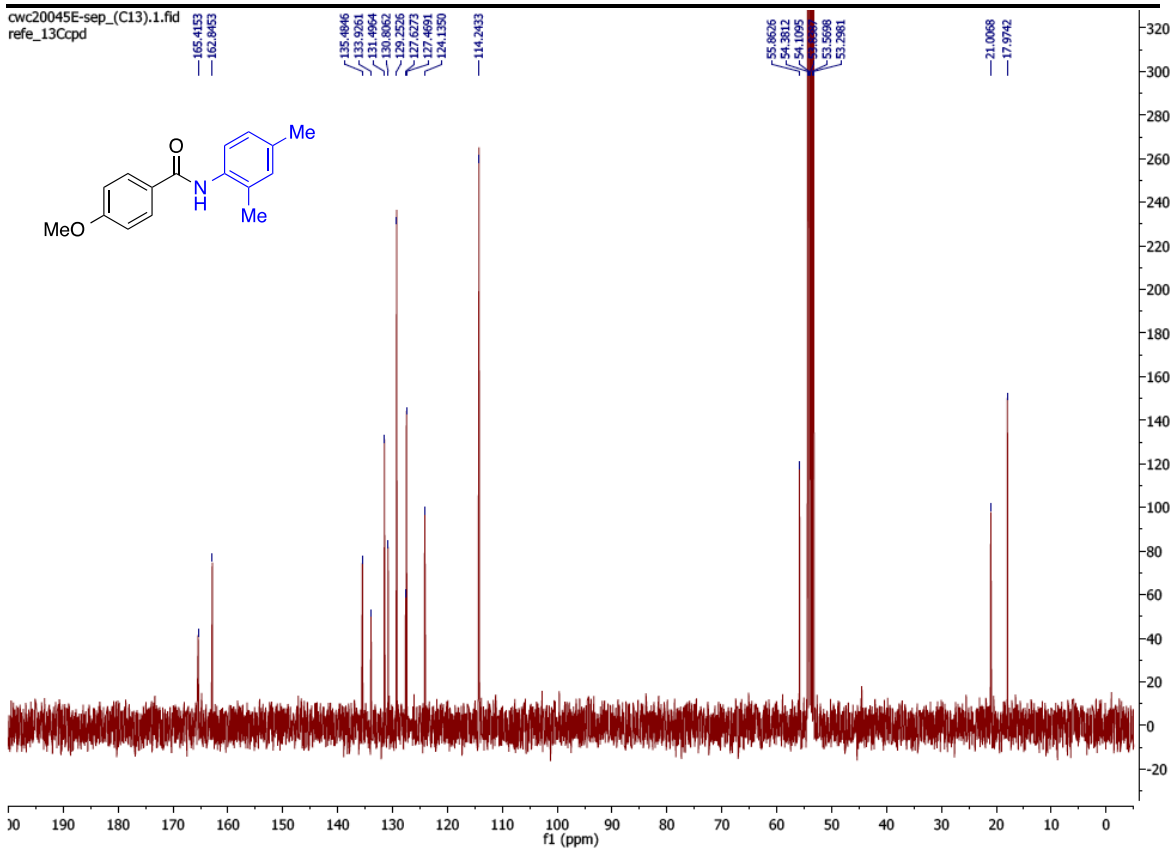
^{1}H and ^{13}C NMR of *N*-(4-(9*H*-Carbazol-9-yl)phenyl)-4-methylbenzamide (4j).





^{1}H and ^{13}C NMR of *N*-(2,4-Dimethylphenyl)-4-methoxybenzamide (4k).





^{1}H and ^{13}C NMR of *N*-(3-methoxy-4-methylphenyl)benzamide (4l).